



Bonding and Integration Technologies for Silicon Carbide Based Injector Components

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Advanced ceramic bonding and integration technologies play a critical role in the fabrication and application of silicon carbide based components for a number of aerospace and ground based applications. One such application is a lean direct injector for a turbine engine to achieve low NO_x emissions. Ceramic to ceramic diffusion bonding and ceramic to metal brazing technologies are being developed for this injector application. For the diffusion bonding, titanium interlayers (PVD and foils) were used to aid in the joining of silicon carbide (SiC) substrates. The influence of such variables as surface finish, interlayer thickness (10, 20, and 50 microns), processing time and temperature, and cooling rates were investigated. Microprobe analysis was used to identify the phases in the bonded region. For bonds that were not fully reacted an intermediate phase, Ti₅Si₃C_x, formed that is thermally incompatible in its thermal expansion and caused thermal stresses and cracking during the processing cool-down. Thinner titanium interlayers and/or longer processing times resulted in stable and compatible phases that did not contribute to microcracking and resulted in an optimized microstructure. Tensile tests on the joined materials resulted in strengths of 13-28 MPa depending on the SiC substrate material. Non-destructive evaluation using ultrasonic immersion showed well formed bonds. For the joining technology of brazing Kovar fuel tubes to silicon carbide, preliminary development of the joining approach has begun. Various technical issues and requirements for the injector application are addressed.



Bonding and Integration Technologies for Silicon Carbide Based Injector Components

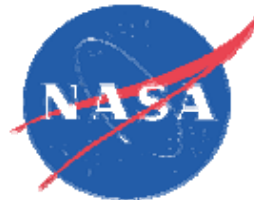
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VEHICLE TECHNOLOGY DIRECTORATE



32nd International Conference & Exposition on Advanced Ceramic & Composites,
Daytona Beach, Florida, Jan. 27- Feb. 1, 2008.



Outline

- **Application** – Micro-Electro-Mechanical Systems Lean Direct Injector (MEMS LDI) for Advanced Aircraft Gas Turbines
- **Joint Processing** - Diffusion Bonding With a Titanium Interlayer
- **Characterization** – SEM, Microprobe, NDE, Pull Tests
- **Near Term Plans** – Subcomponent Fabrication
- **Brazing** – Kovar to SiC
- **Summary and Conclusions**



Motivation

Improve Ceramic to Ceramic and Ceramic to Metal Joining Methods

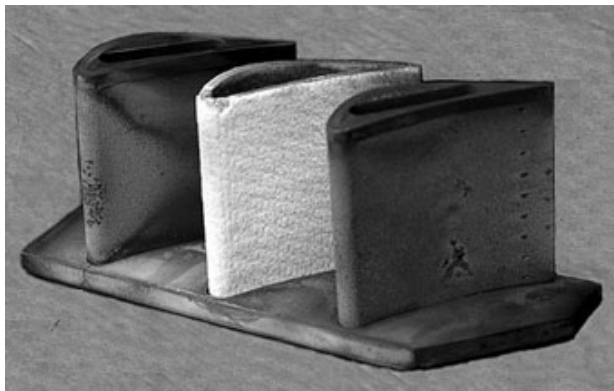
- allow for the fabrication of complex shapes and structures.
- allow for easier integration of ceramics components into engine systems.

(Ceramics can be either monolithics or fiber reinforced composites).

Examples of Component Applications Benefiting from Joining Technology

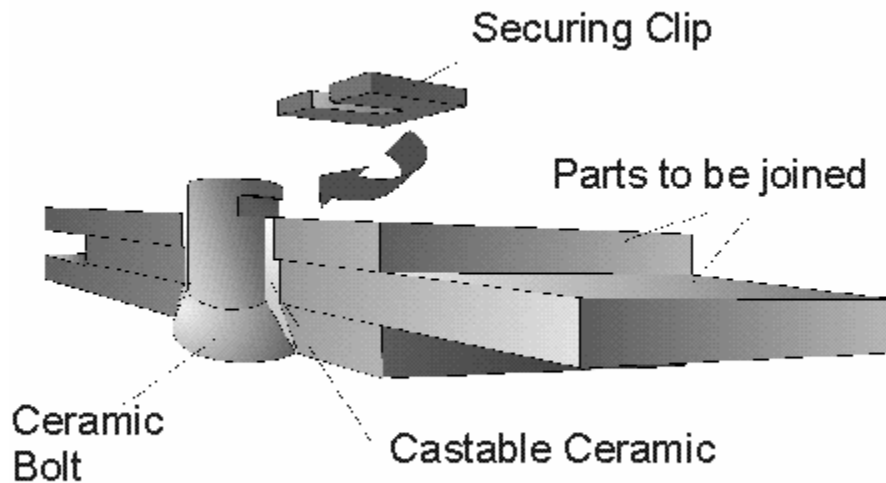
– components for aeronautic and ground based engine applications (i.e. ceramic turbine vanes, blades, injectors, rotors, combustor liners, valves, and heat shields) and fusion reactor components, optical space components, and bi-layer armor.

Benefits – simplified component fabrication, enabling technology, increased operating temperatures, improved efficiency, and reduced cooling requirements.





Joining Approaches - Mechanical Fasteners



Plates Joined with Mechanical Fasteners

Issues with Mechanical Fasteners

- Difficult and costly to machine fastener parts
- Articles to be joined must have holes machined
- Limited material options for commercially available mechanical fasteners
- Must be chemically and thermally compatible with the articles to be fastened
- High mechanical and thermal loads on the fastener
- Slots require tight tolerances and must be airtight



Mechanical Fasteners

A wide variety of ceramic nuts, bolts, and washers can be made out of alumina or zirconia.



Joining Approaches– Chemical Joining

- **Fusion Welding** – mating surface regions of components are melted and mixed before solidifying to form a permanent bond.
- **Brazing** – liquid metal flows into a narrow gap between the mating surfaces and solidifies to form a permanent bond.
- **Glazing and Glass Sealing** – uses a fluid glass to bond mating surfaces in processes analogous to brazing or fusion welding.
- **Adhesive Bonding** – component gaps are filled by fluid organic compounds that polymerize to form rigid bonding interlayers.
- **Diffusion Bonding** – mating surfaces are pressed together and heated to cause bonding by interdiffusion of the components.
- **High Temperature Reactive Joining** - reactive formation of high temperature capable joints (ARCJoinT).

Focus of Current Efforts on Diffusion Bonding Using a Ti Interlayer

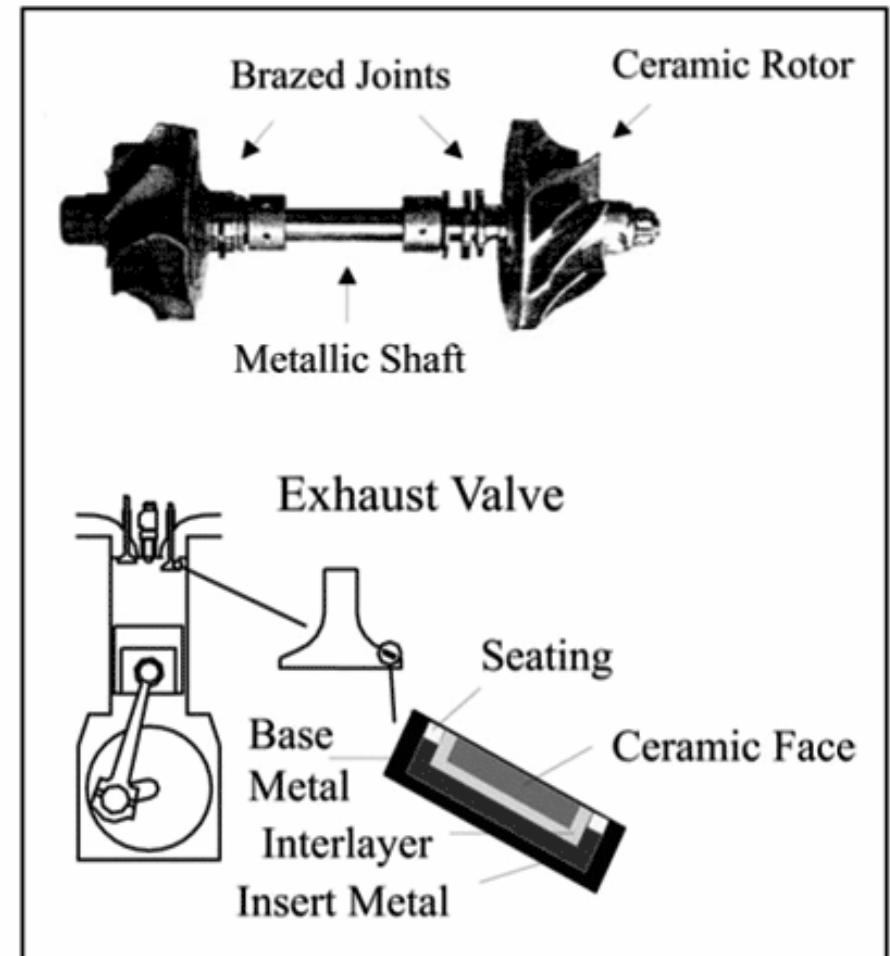


Joining Approaches

Examples of Complex Shapes and Components



Examples of SiC ceramics and composite sub-elements joined using ARCJoinT (Jay Singh, NASA GRC)

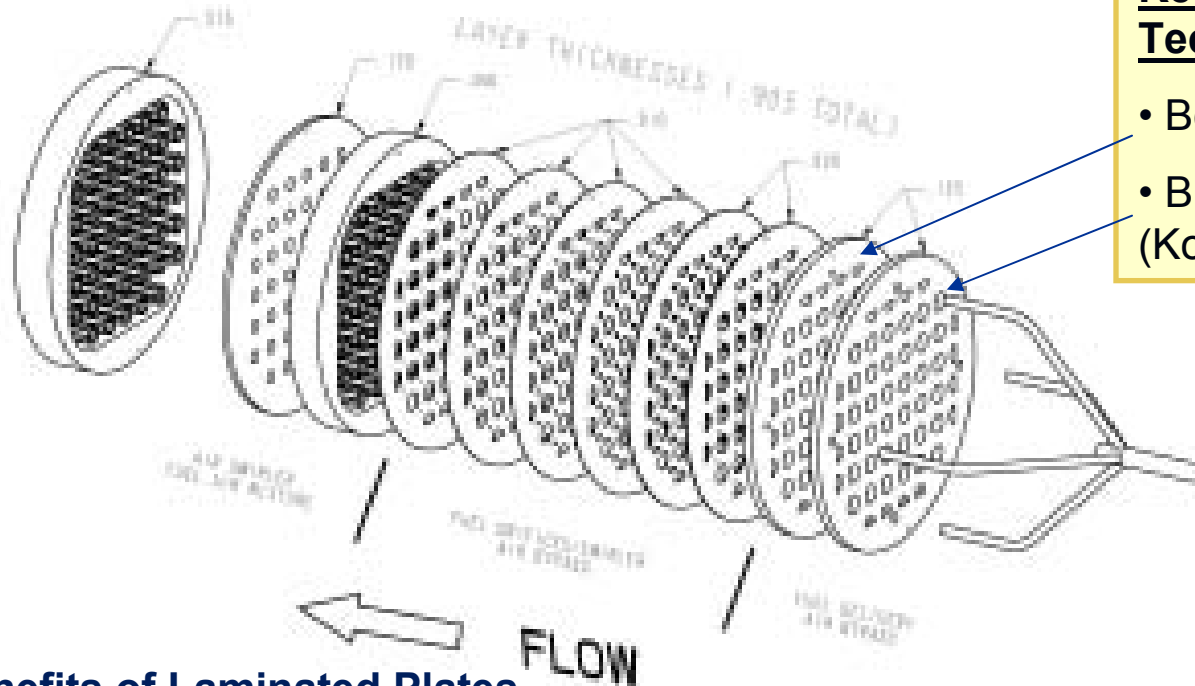


Nascimento et al, Cerâmica vol.49 no.312



Fabrication of Lean Direct Injector Components by Diffusion Bonding of SiC Laminates

SiC laminates can be used to create intricate and interlaced passages to speed up fuel-air mixing to allow lean-burning, ultra-low emissions



Key Enabling Technologies:

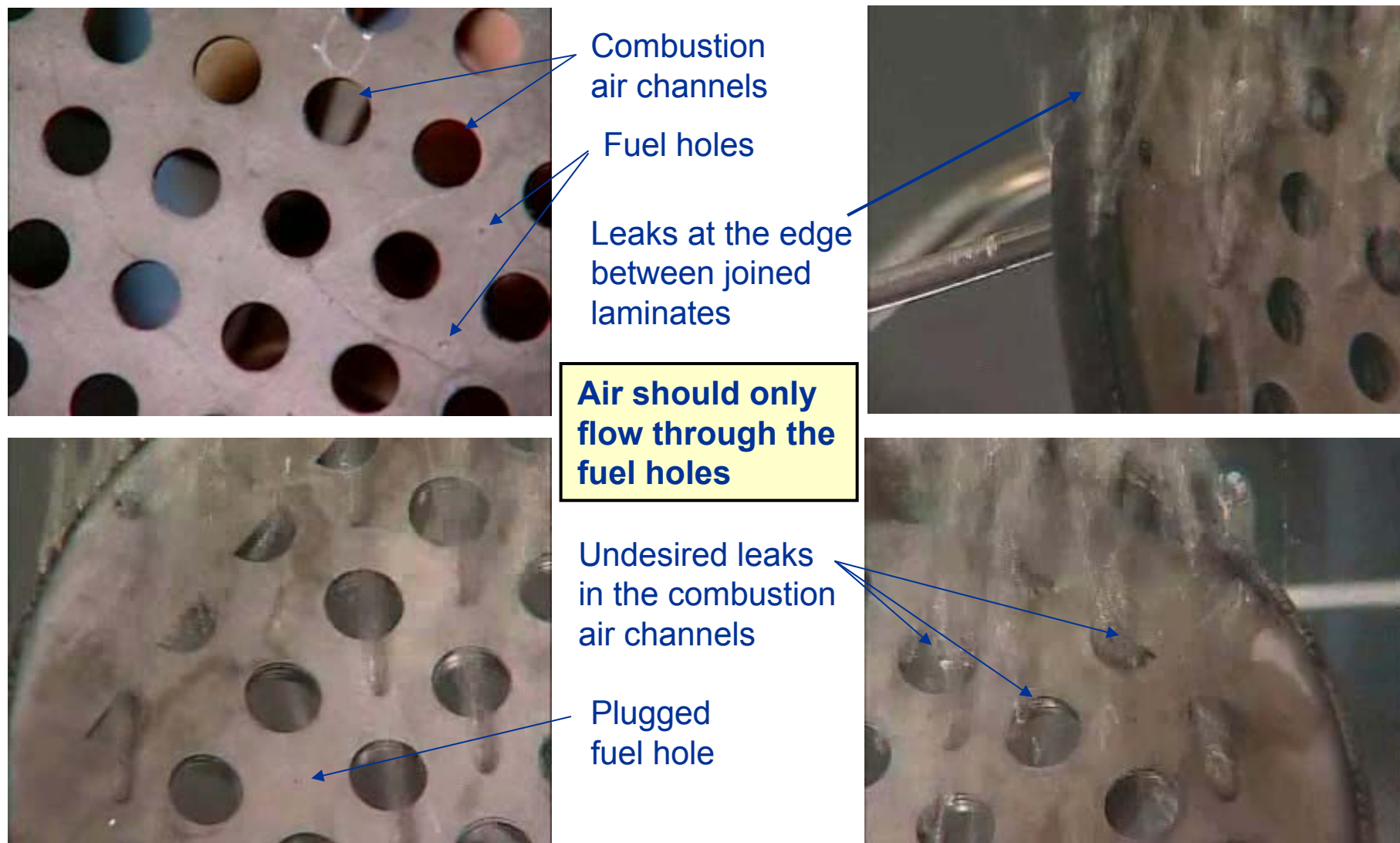
- Bonding of SiC to SiC
- Brazing of SiC to Metallic (Kovar) Fuel Tubes

Benefits of Laminated Plates

- Passages of any shape can be created to allow for multiple fuel circuits
- Provides thermal protection of the fuel to prevent choking
- Low cost fabrication of modules with complicated internal geometries through chemical etching



Leak Test of SiC Laminates Joined with Silicate Glass





Previous Approach of Joining SiC With a Silicate Glass Layer

Leak Test
Movie



Movie Courtesy of
Chip Redding at
NASA GRC

Disadvantages of Joining Silicon Carbide with a Silicate Glass Layer

- Difficult to achieve a uniform layer
- Relatively low strength
- Glass flows and fills in holes and edges where it is not desired
- Glass joints were not leak-free



Current Approach of Joining SiC With a Ti Layer

Advantages of Diffusion Bonding Using a Ti Layer

- Uniform Ti layers can be applied
- Ti can be applied by different methods (foil, PVD and other coating approaches)
- High strength and leak-free bonds
- Good high temperature stability

The objective is to develop joining technology that has the following capabilities necessary for the injector application:

- Joining of relatively large geometries (i.e. 4" diameter discs)
- Leak-free at an internal pressure of 200 psi (1.38 MPa)
- Stability and strength retention at 800°F (427°C)



SiC-Ti-SiC Diffusion Bond Processing Matrix

- first processing matrix investigated

SiC and Ti Material Combinations:

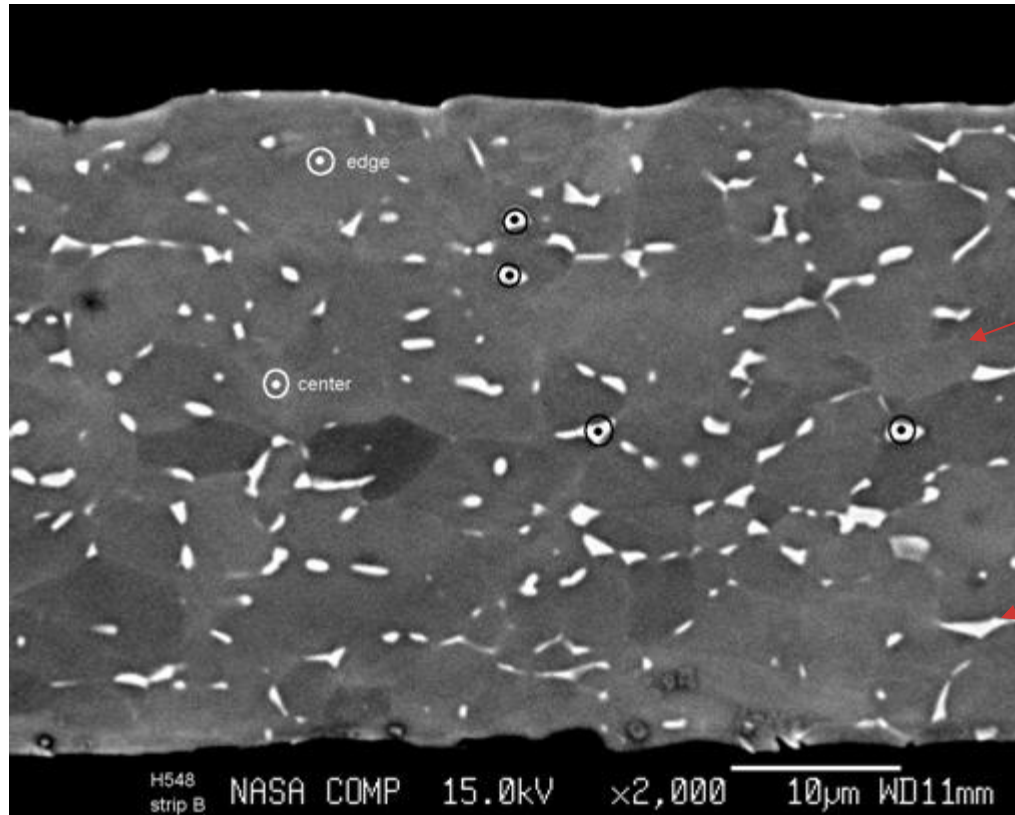
1. 1.75" diameter α -SiC (CRYSTAR from Saint-Gobain) discs joined with a 38 micron alloyed Ti foil
2. 1.75" diameter CVD SiC (TREX Enterprises) discs joined with a 38 micron alloyed Ti foil
3. 1" x 2" CVD SiC (Rohm & Hass) coupons joined with ~10 micron PVD Ti coating on one of the surfaces
4. 1" x 2" CVD SiC (Rohm & Hass) coupons joined with a 38 micron alloyed Ti foil
5. 1" x 2" CVD SiC (Rohm & Hass) coupons joined with ~10 micron PVD Ti coating on both of the surfaces (20 micron total PVD Ti)

Condition	Temp. (°C)	Pressure* (MPa)	Time (hr)	Atmosphere	Cooling Rate (°C/min)	Analysis
A (materials 1, 2, and 3)	1250	24, 24, 31	2	vacuum	5	Microscopy & Microprobe
B (materials 1 and 3)	1300	24, 31	2	vacuum	2	Microscopy
C (materials 1 and 3)	1250	50	2	vacuum	2	Microscopy
D (materials 1, 4 and 5)	1250	24, 31	2	vacuum	2	Microscopy & Microprobe
*at minimum clamping pressure for the hot press						



Alloyed Ti Foil

Ti-6Al-4V (weight %)



Grey phase – Alpha alloy

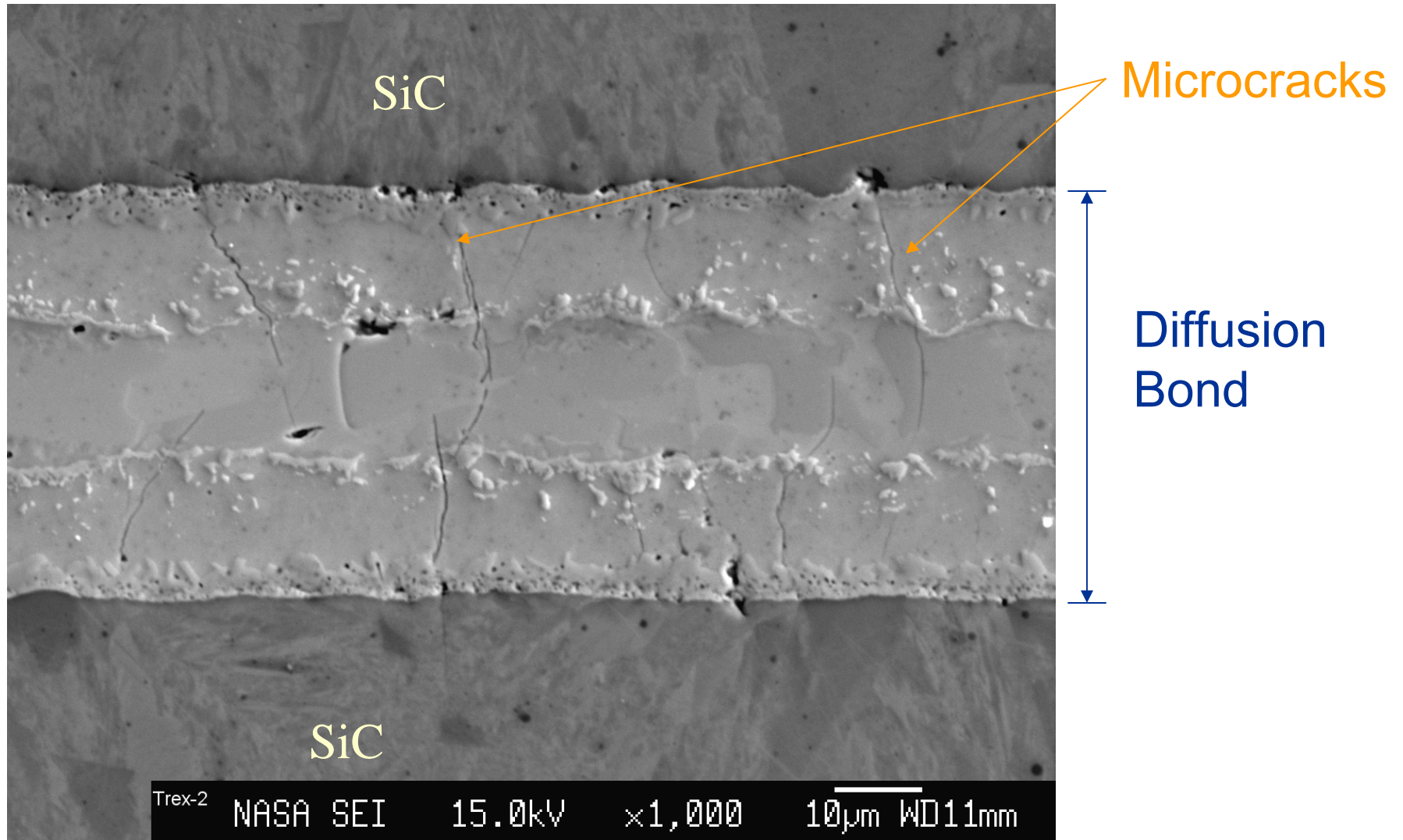
White phase – Beta alloy

Microprobe from the cross-section of alloyed Ti foil (averages taken from several points near the edge and at the center of the foil)

	Phase	Al	Fe	Ti	V	Total
Atomic Ratio	Grey Phase	10.196	0.042	86.774	2.988	100.000
Weight (%)	Grey Phase	5.999	0.051	90.632	3.318	100.000
Atomic Ratio	White Phase	4.841	1.850	76.507	16.803	100.000
Weight (%)	White Phase	2.748	2.172	77.084	17.997	100.000



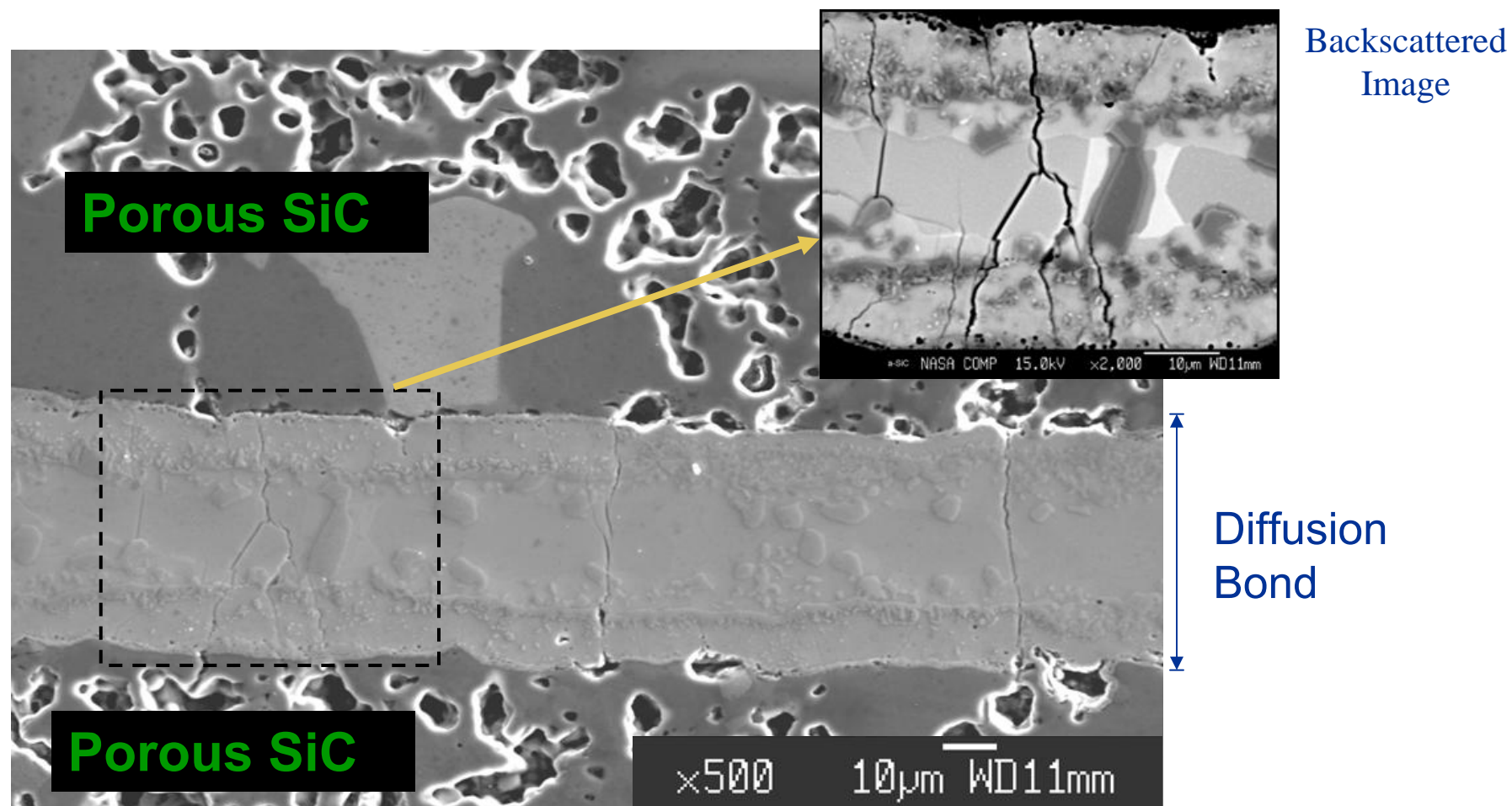
Secondary Electron Image of the Diffusion Bond Alloyed Ti Foil and Trex CVD SiC





Secondary Electron Image of the Diffusion Bond

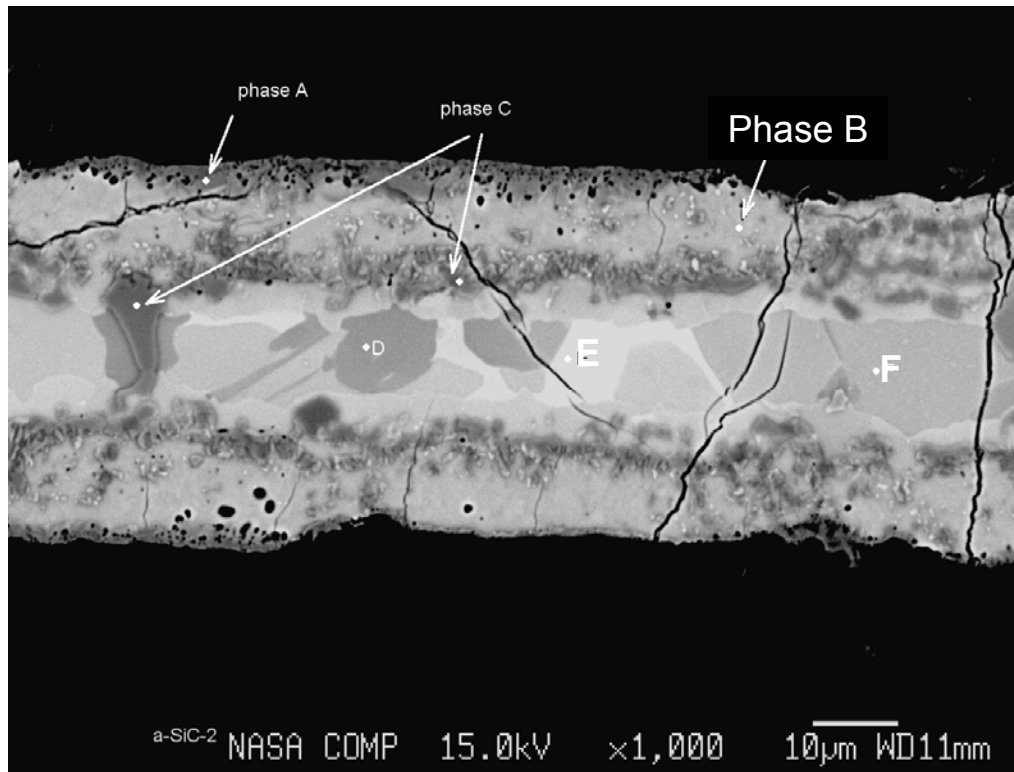
Alloyed Ti Foil and Alpha-SiC





Microprobe of α -SiC Reaction Bonded Using Ti Foil

Conditions: 1250 °C, 24 MPa, 2 hr, vacuum, 5 °C/min



Microcracking may be due to thermal stresses during cooling down from processing:

Phase B $\text{Ti}_5\text{Si}_3\text{C}_x$ (Ti_5Si_3) is highly anisotropic in its thermal expansion where $\text{CTE}(c)/\text{CTE}(a) = 2.72$ (Schneibel et al).

Phase E is a beta Ti alloy phase and phase F is an alpha Ti alloy phase.

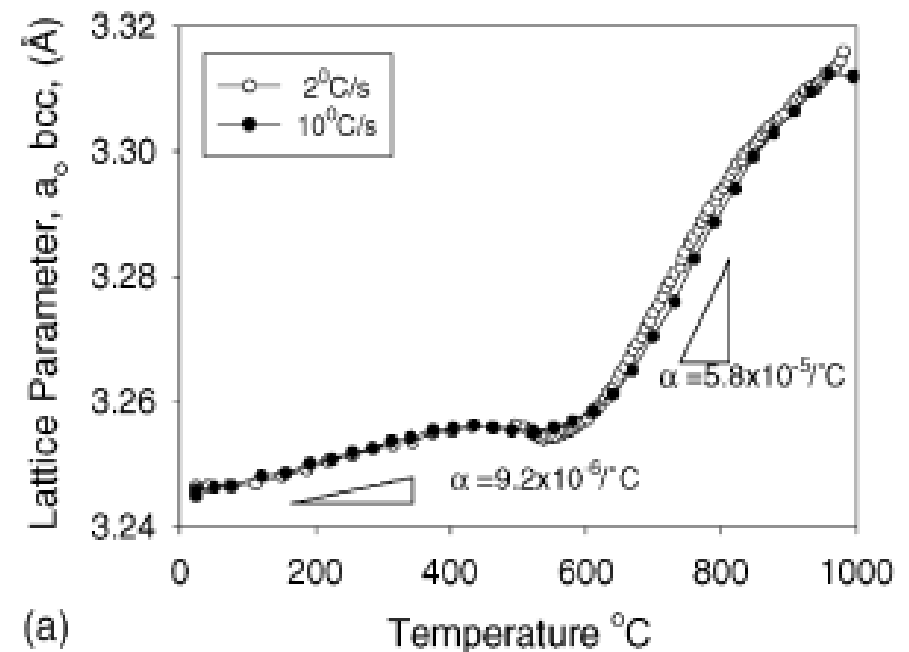
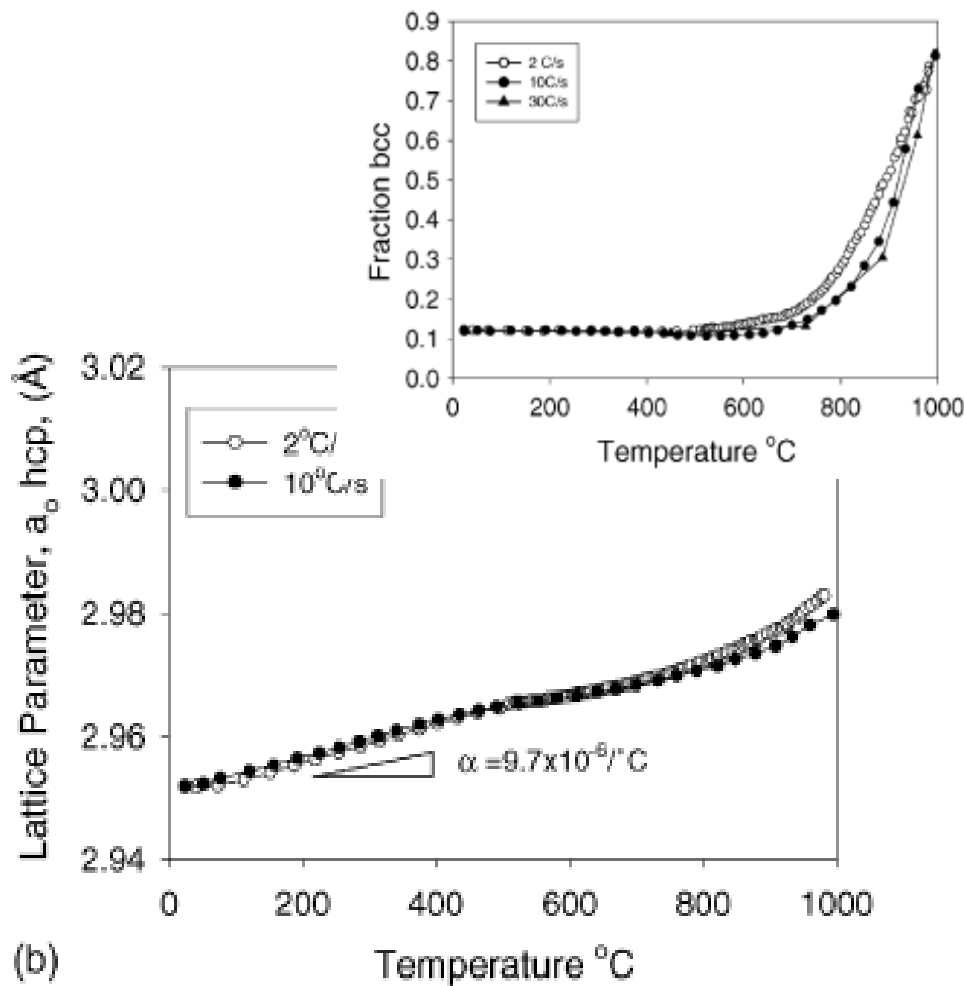
Alpha-SiC and alloyed Ti foil - Atomic Ratios

Phase	Al	V	Cr	Si	C	Ti	Fe	Total
Phase A	0.020	0.970	0.023	7.662	34.787	56.531	0.007	100.000
Phase B	0.076	0.923	0.020	34.151	6.502	58.220	0.108	100.000
Phase C	0.223	0.760	0.019	6.015	32.269	60.690	0.025	100.000
Phase D	21.862	2.363	0.050	0.432	10.394	64.865	0.036	100.000
Phase E	27.102	21.318	0.611	0.473	1.901	46.456	2.141	100.000
Phase F	25.975	5.962	0.145	1.186	1.898	64.666	0.168	100.000

Thermal Expansion Issues for the Alpha and Beta Ti Alloy Phases



From Elmer et al, Materials Science and Engineering A 391 (2005) 104-113.

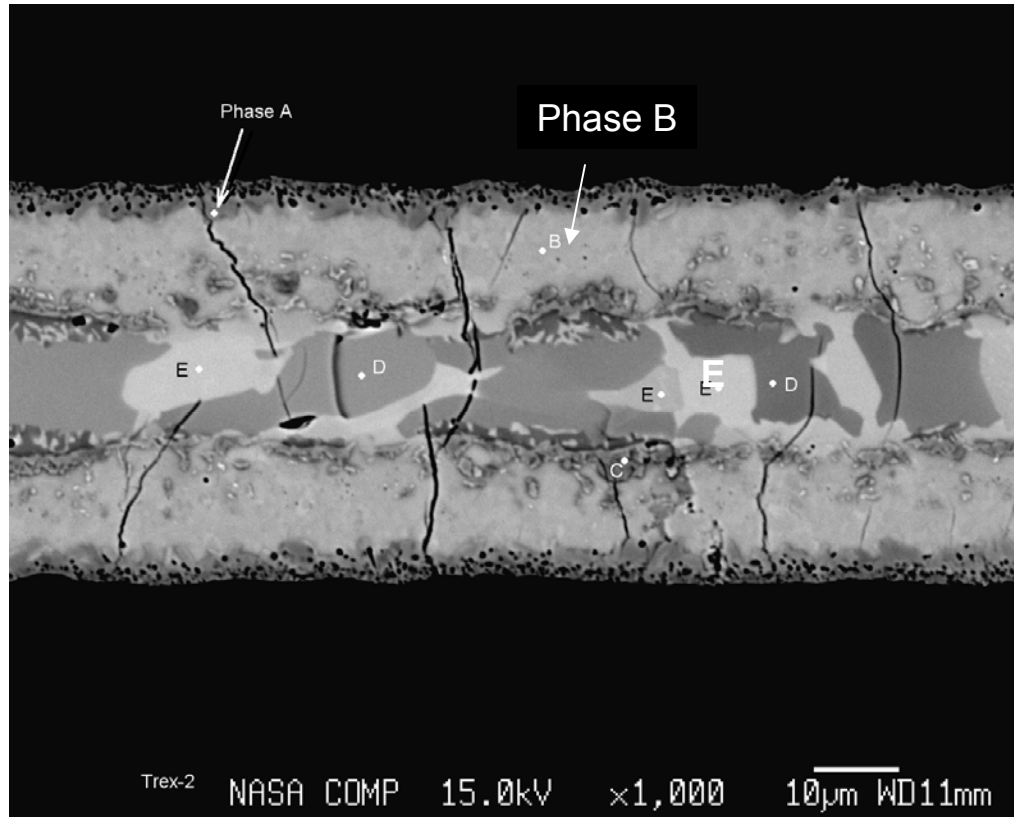


- Central core of diffusion bond has concentrated alpha and beta Ti alloy phases. The alpha phase has an anisotropic thermal expansion which is 20 % greater along the c-axis (Boyer, Welsch, and Colling). Also, the beta phase has a thermal expansion that is 6 x higher in the temperature range of 600-1000°C ($5.8 \times 10^{-5} / ^\circ\text{C}$) compared the thermal expansion below 600°C ($9.2 \times 10^{-6} / ^\circ\text{C}$) (Elmer et al).



Microprobe of TREX CVD SiC Reaction Bonded Using Ti Foil

Conditions: 1250 °C, 24 MPa, 2 hr, vacuum, 5 °C/min



Microcracking is observed and the following phases are likely contributors:

Phase B: $\text{Ti}_5\text{Si}_3\text{C}_x$ (Ti_5Si_3)

Phase E: beta Ti alloy phase

(microprobe analysis may have missed the presence of an alpha Ti alloy phase)

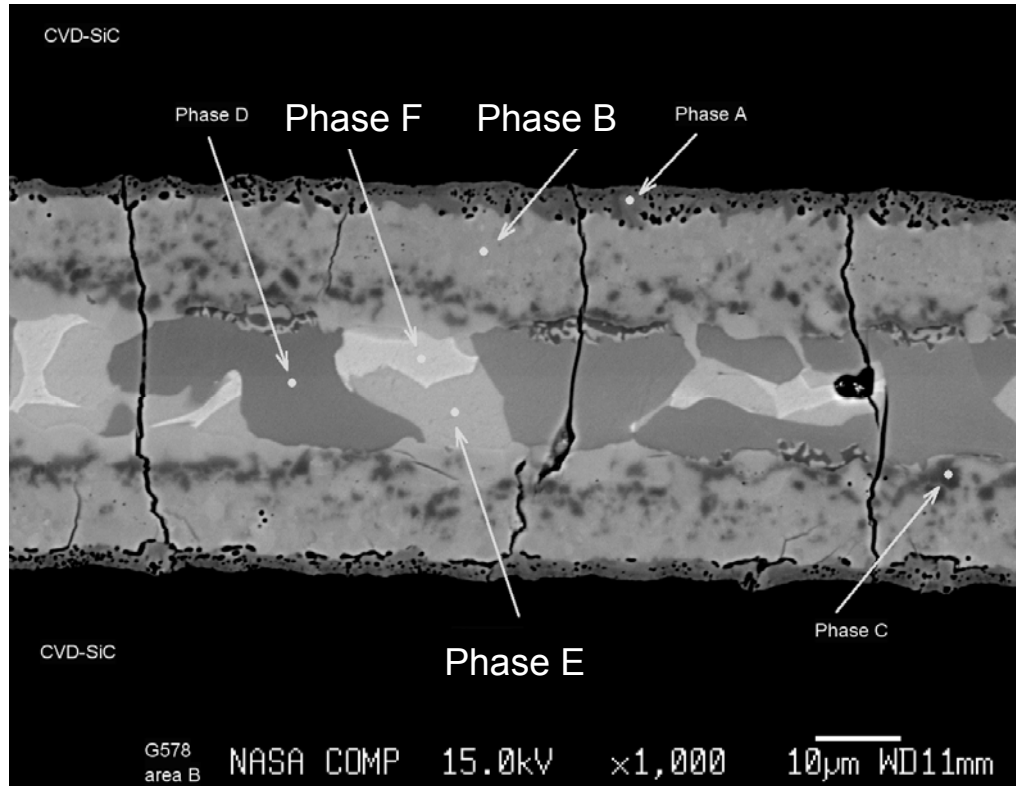
TREX SiC and alloyed Ti foil - Atomic Ratios

Phase	Al	V	Cr	Si	C	Ti	Fe	Total
Phase A	0.101	0.578	0.026	18.733	24.317	56.243	0.004	100.000
Phase B	0.384	1.220	0.025	34.639	6.904	56.794	0.034	100.000
Phase C	0.604	0.715	0.023	3.148	35.366	60.124	0.020	100.000
Phase D	19.887	1.424	0.026	0.537	13.719	64.381	0.025	100.000
Phase E	26.941	14.935	0.396	0.588	0.747	55.684	0.710	100.000



Microprobe of Rohm & Haas SiC Reaction Bonded Using Ti Foil

Conditions: 1250 °C, 24 MPa, 2 hr, vacuum, 2 °C/min



Microcracking is again observed and the following phases are likely contributors:

Phase B: $\text{Ti}_5\text{Si}_3\text{C}_x$ (Ti_5Si_3)

Phase E: alpha Ti alloy phase

Phase F: beta Ti alloy phase

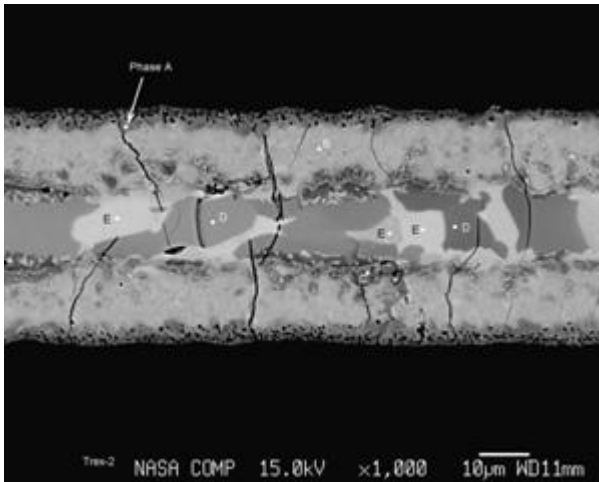
Rohm & Haas CVD SiC and Alloyed Ti Foil - Atomic Ratios

Phase	Al	V	Cr	Si	C	Ti	Fe	Total
Phase A	0.070	0.848	0.030	17.085	25.802	56.164	0.001	100.000
Phase B	0.303	0.961	0.018	33.766	6.675	58.212	0.064	100.000
Phase C	0.293	0.661	0.010	5.234	35.671	58.122	0.010	100.000
Phase D	19.002	1.392	0.039	0.557	12.707	66.288	0.014	100.000
Phase E	23.244	7.649	0.213	0.758	3.970	64.104	0.062	100.000
Phase F	19.833	20.784	0.634	0.514	4.622	52.302	1.313	100.000

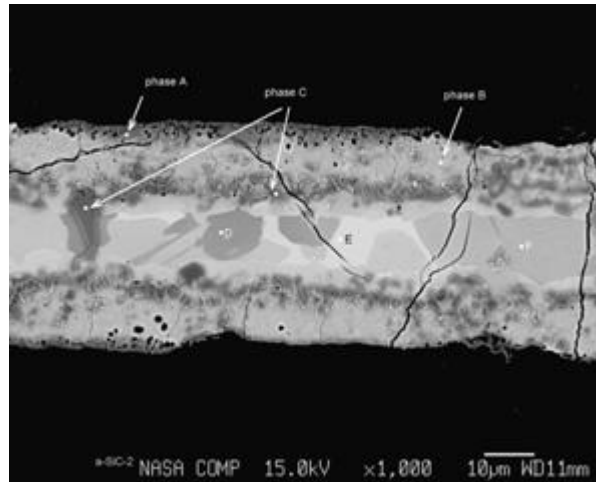


Summary of Diffusion Bonds Formed With Alloyed Ti Foil Interlayers Between Different SiC Substrates

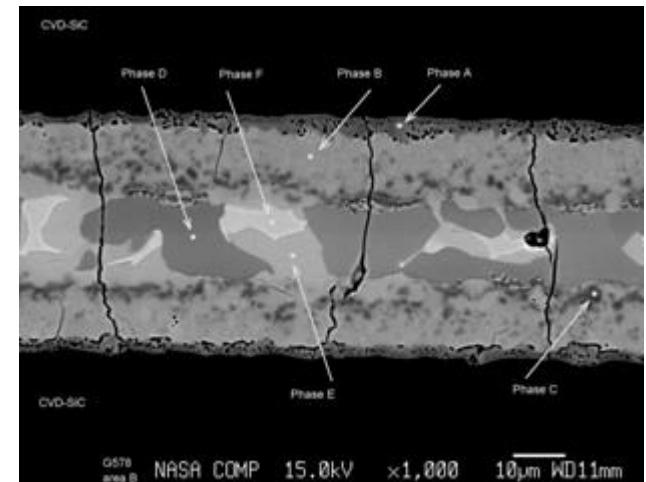
TREX CVD SiC



CRYSTAR α -SiC



Rohm & Haas CVD SiC



Microcracks formed regardless of the substrate and variations in the processing: higher temperatures, higher pressures, slower cooling rate.

Microcracking is very likely due to thermal stresses during cooling down from processing.

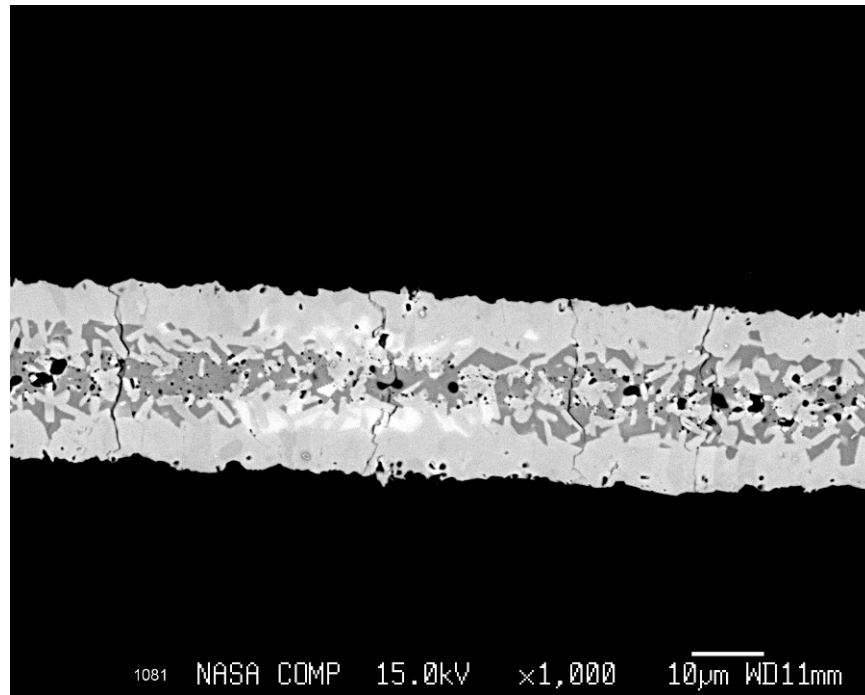
The CTE issues of the alpha and beta Ti alloy phases can be avoided if pure Ti is used.

The anisotropic $Ti_5Si_3C_x$ phase could possibly be avoided with different processing conditions.

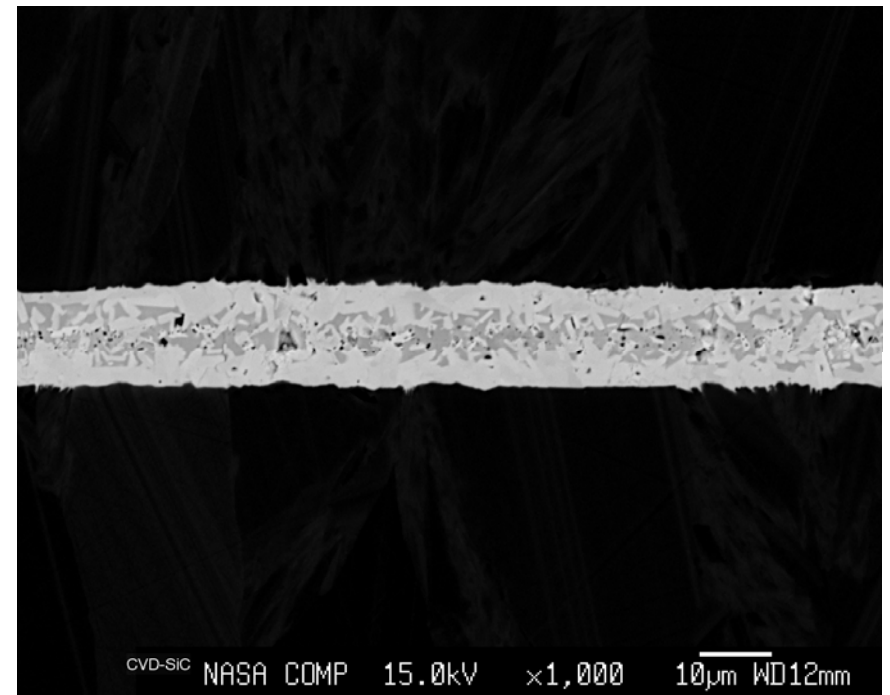


Diffusion Bonds from Using PVD Ti as the Interlayer

20 Micron Ti Interlayer



10 Micron Ti Interlayer

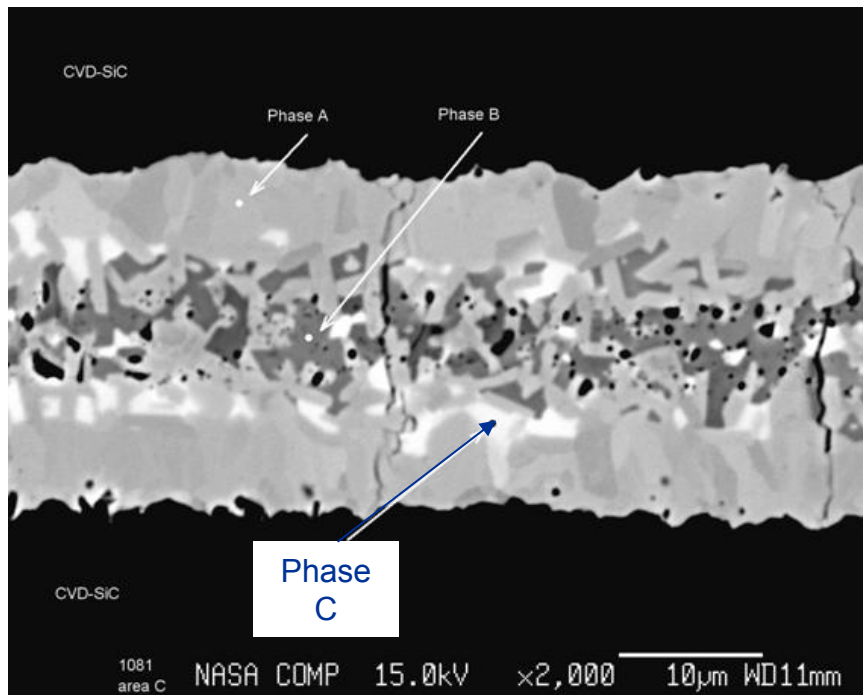


Diffusion Bonds from Using PVD Ti as the Interlayer

20 Micron Ti Interlayer

Microcracking is still present due to the presence of $\text{Ti}_5\text{Si}_3\text{C}_x$.

Naka et al suggest that this is an intermediate phase.



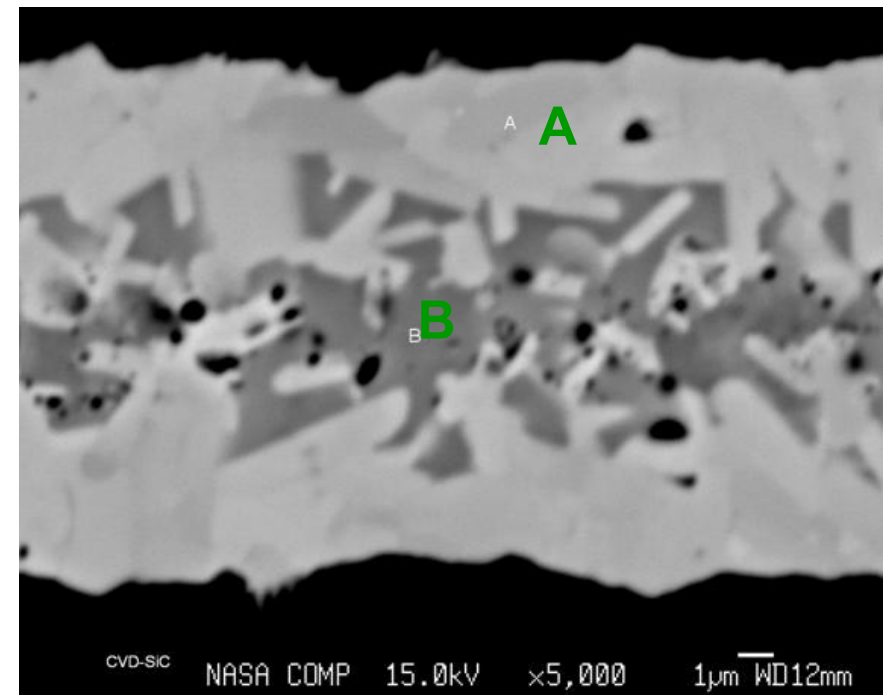
Phases in bond with the 20 μ Ti Interlayer – Atomic Ratios

Phase	Ti	Si	C
Phase A	56.426	17.792	25.757
Phase B	35.794	62.621	1.570
Phase C	58.767	33.891	7.140

10 Micron Ti Interlayer

No microcracking or phase of $\text{Ti}_5\text{Si}_3\text{C}_x$ is present.

Thin interlayers of pure Ti down-selected as the preferred interlayer.



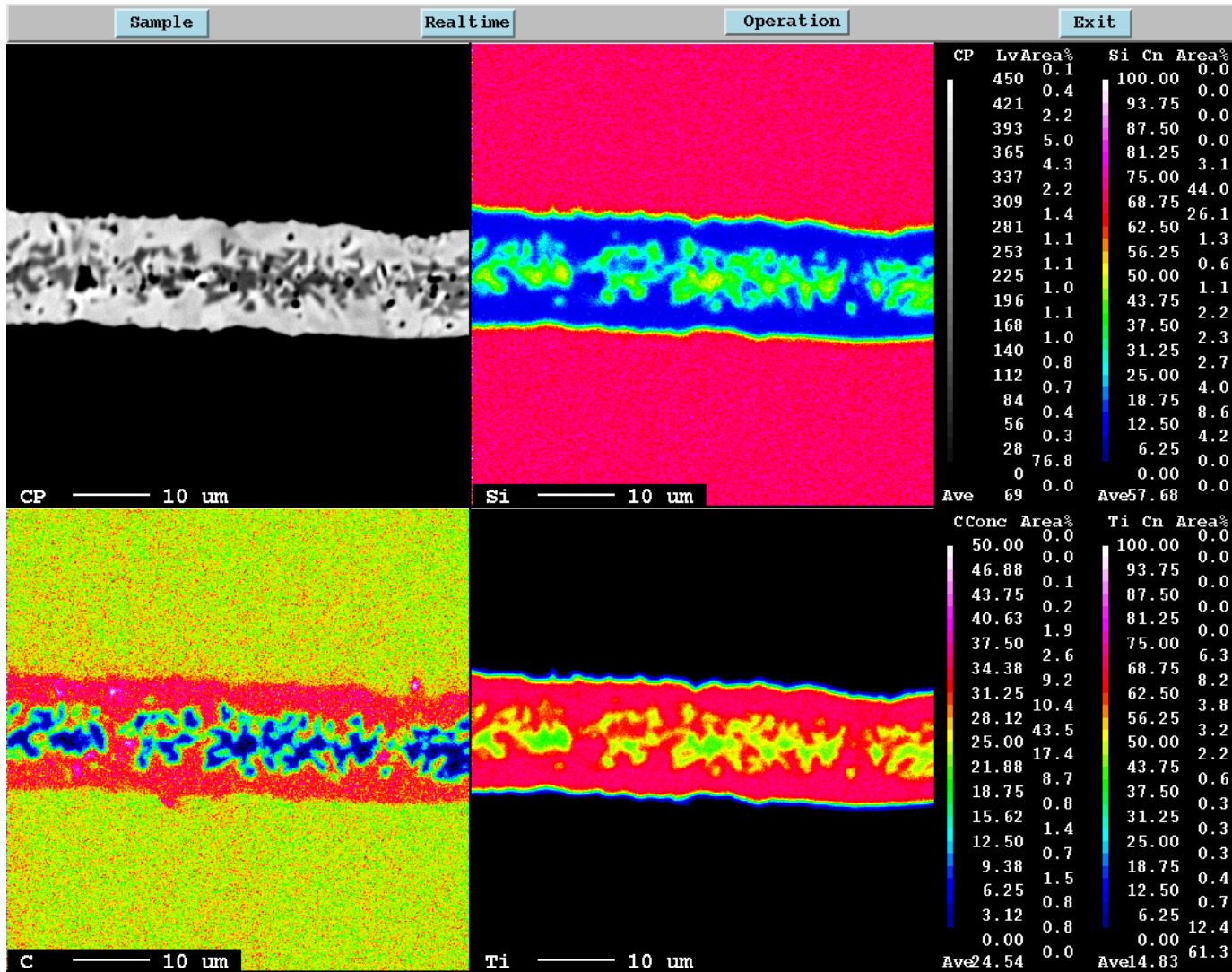
Phases in bond with the 10 μ Ti Interlayer – Atomic Ratios

Phase	Ti	Si	C
SiC	0.011	54.096	45.890
Phase A	56.621	18.690	24.686
Phase B	35.752	61.217	3.028



Microprobe of CVD SiC Reaction Bonded Using PVD Ti

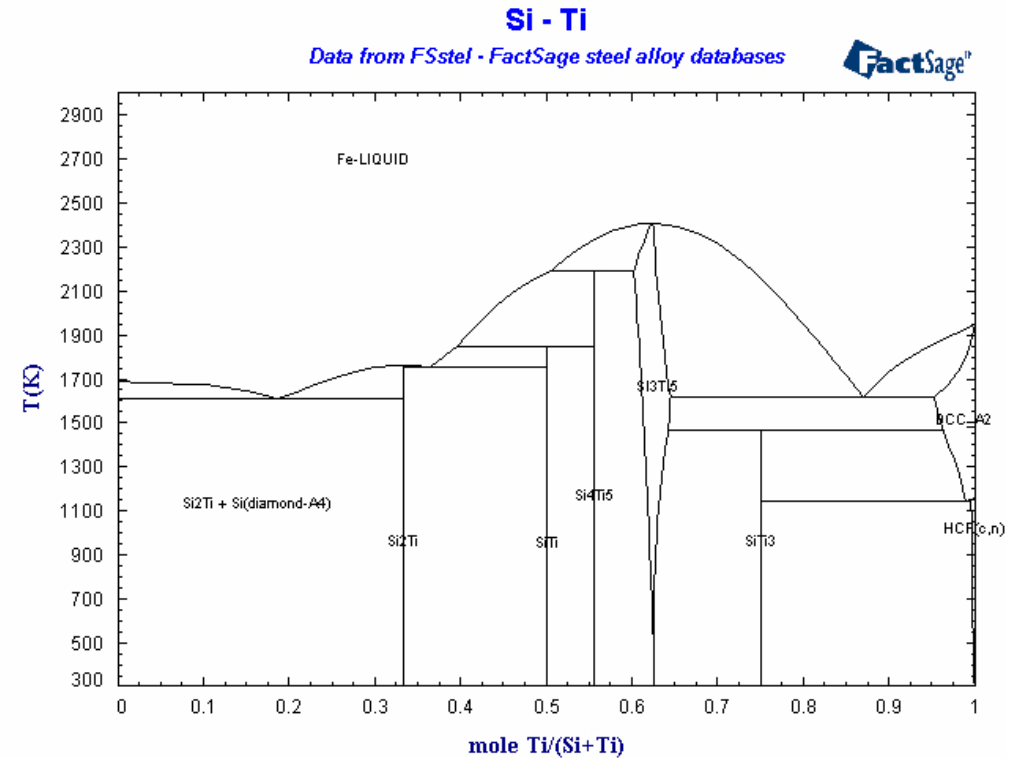
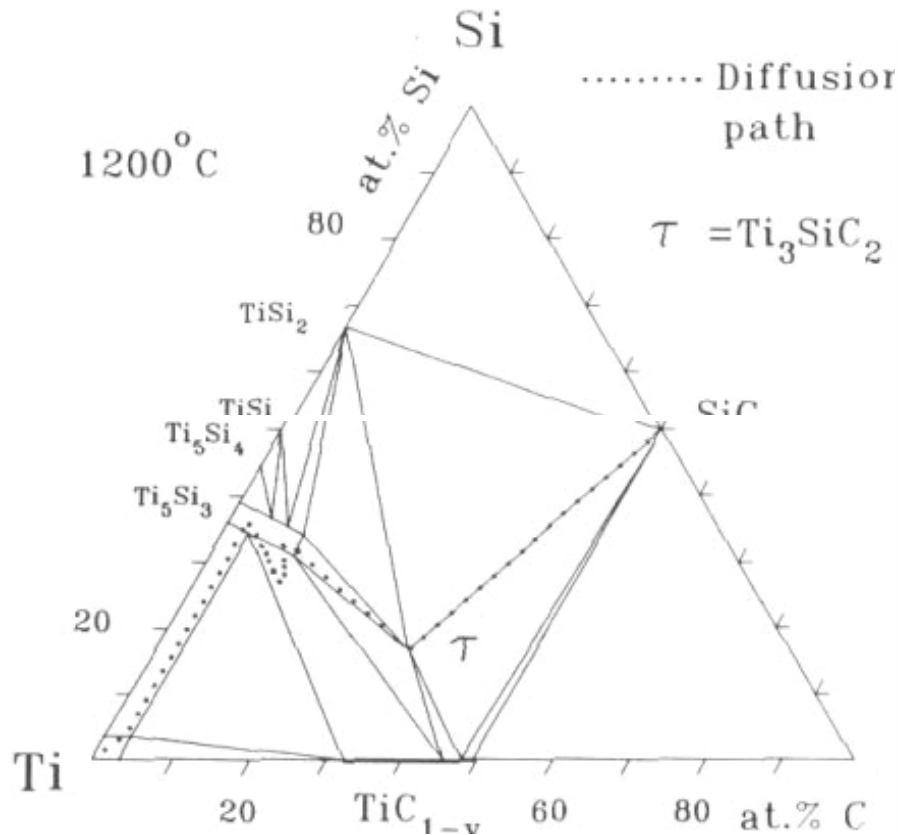
Conditions: 1250 °C, 31 MPa, 2 hr, vacuum, 5 °C/min



The use of a high purity, thin Ti interlayer contributed to a less complex diffusion bond.



The Phases of Ti-Si-C and the Intermediate Phase of Ti_5Si_3



An isothermal section of the Ti-Si-C phase diagram at 1200°C. The diffusion path is denoted by the dotted line. SiC/ Ti_3SiC_2 / Ti_5Si_3 /two-phase Ti_5Si_3 plus TiC_{1-y} / Ti_5Si_3 /Ti

F. Goesmann and R. Schmid-Fetzer, Semicond. **Sd. Technol.** **10** (1995) 1652-1658.



Effect of Ti Foil Thickness and Processing Time on the Resulting Diffusion Bonds

- second processing matrix investigated

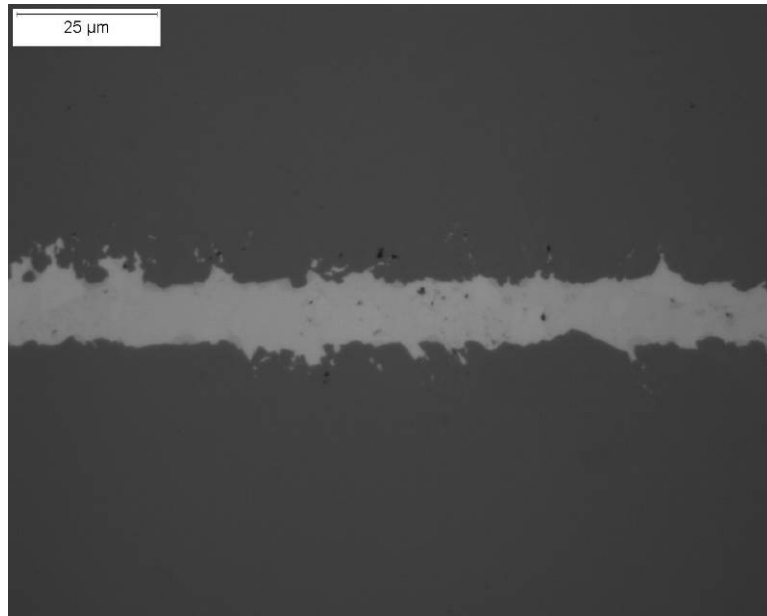
The following conditions were investigated:

- 10 micron foil at 2 hr
- 20 micron foil at 1, 2, and 4 hr
- 50 micron foil at 1, 2, 4, 8 and 16 hr

* all other conditions are the same as before: 1250 °C, 30 MPa applied pressure, vacuum, 2 °C /min cool down



SiC Substrates Joined with a 10 μm Ti Foil Interlayer for 2 hr

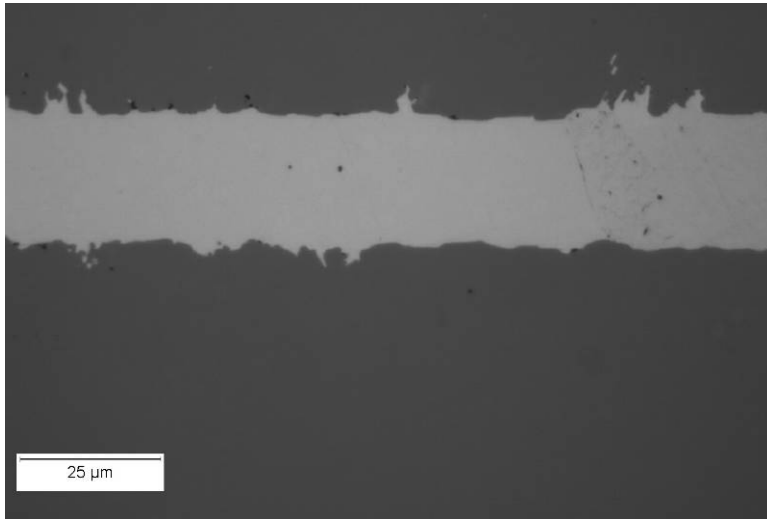


Similar results to the diffusion bond formed with a 10 micron thick PVD Ti coating

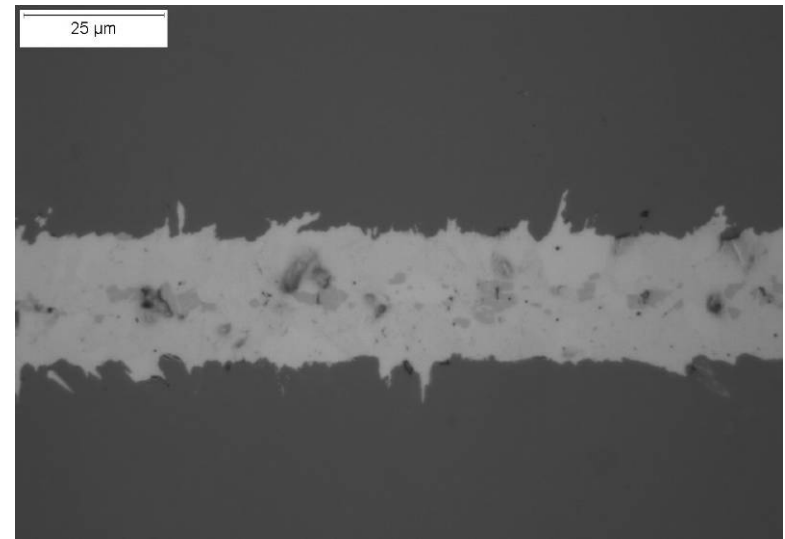
- no microcracks



SiC Substrates Joined with a 25 μm Ti Foil Interlayer



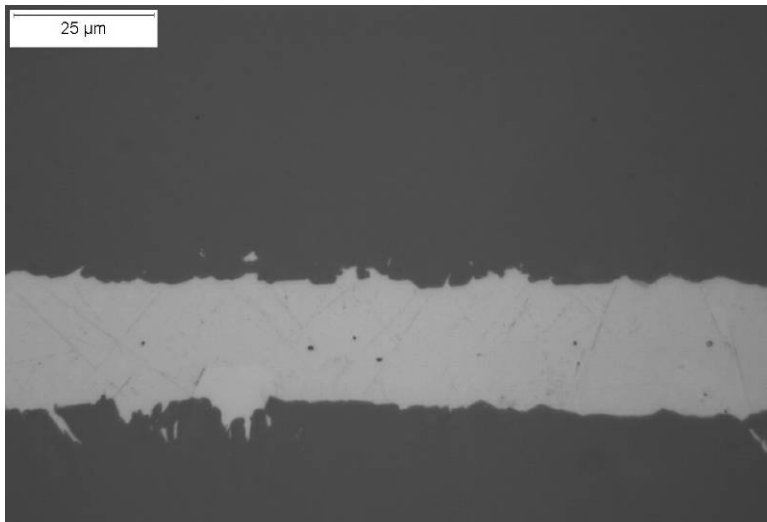
1 hr.



2 hr.

An intermediate phase is observed after 2 hr but not after 4 hr.

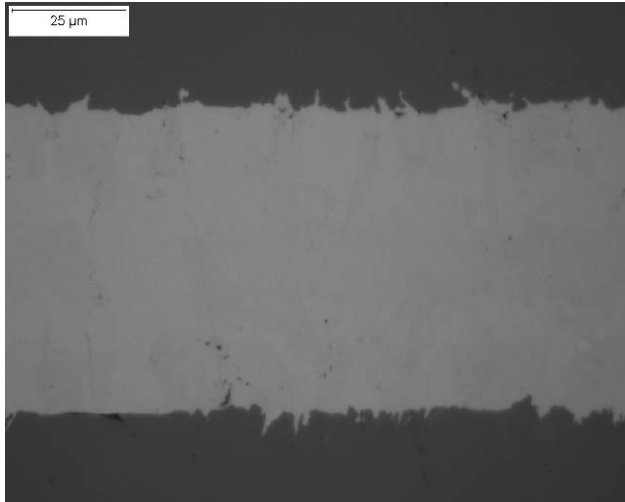
- no microcracks



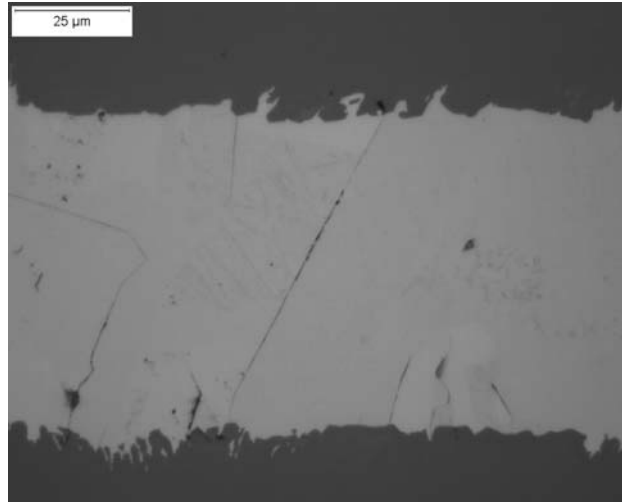
4 hr.



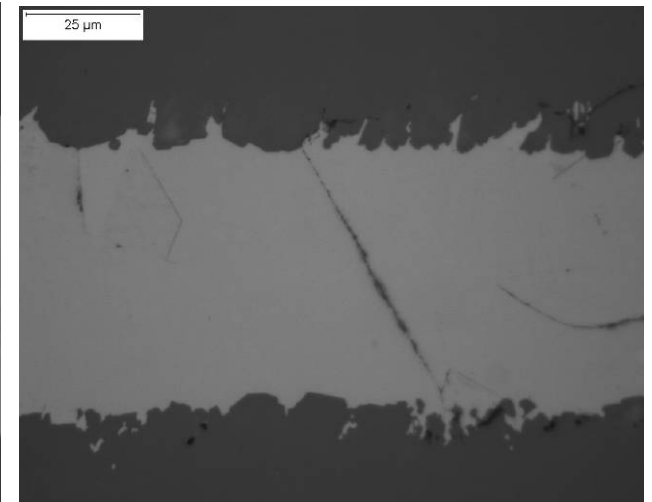
SiC Substrates Joined with a 50 μm Ti Foil Interlayer



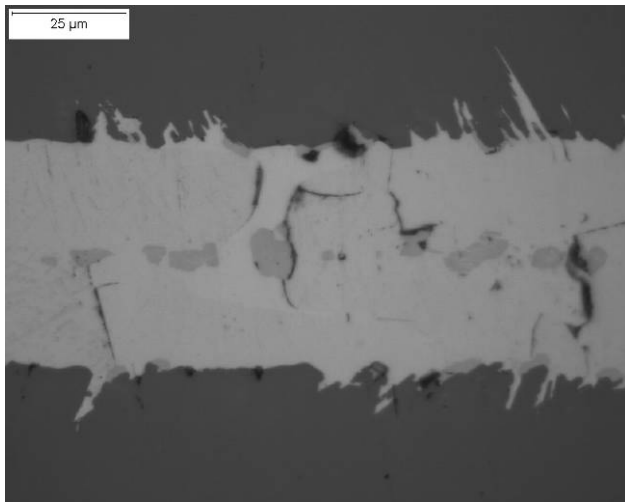
1 hr.



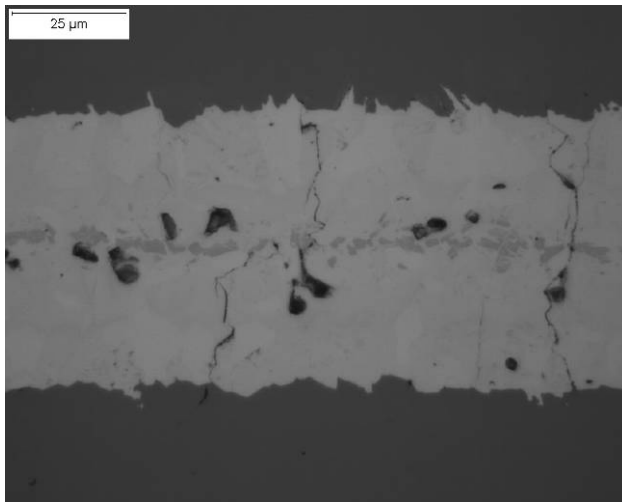
2 hr.



4 hr.



8 hr.



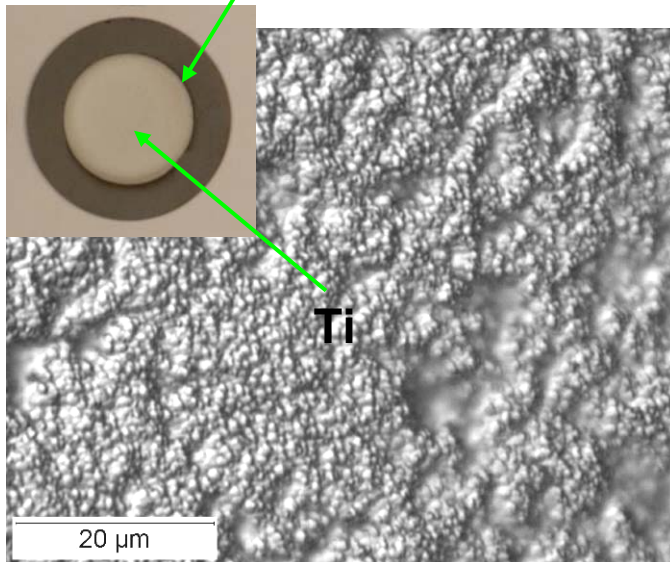
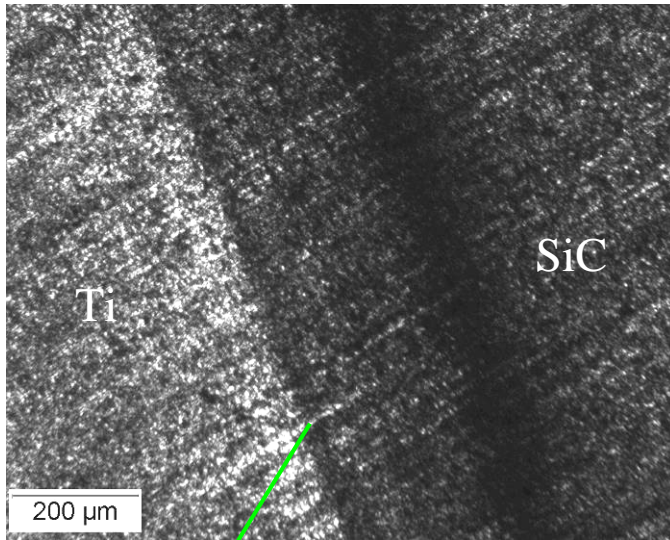
16 hr.

Over time, the formation of microcracks and an intermediate phase are observed followed by void formation and a lessening of the intermediate phase.

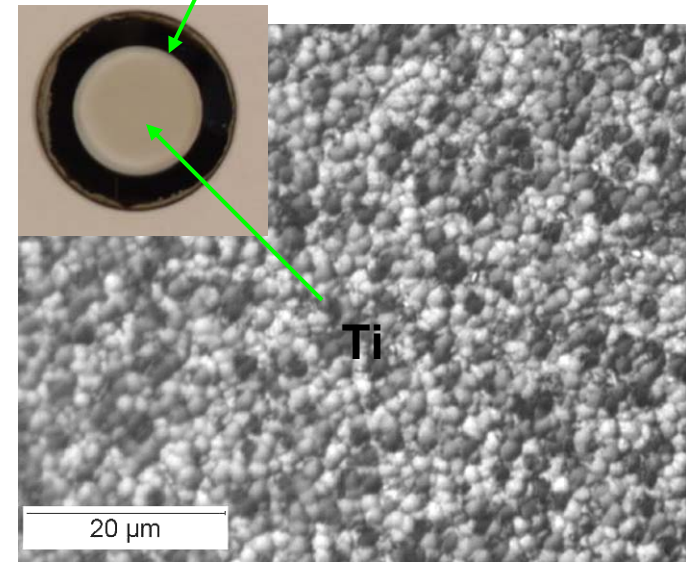
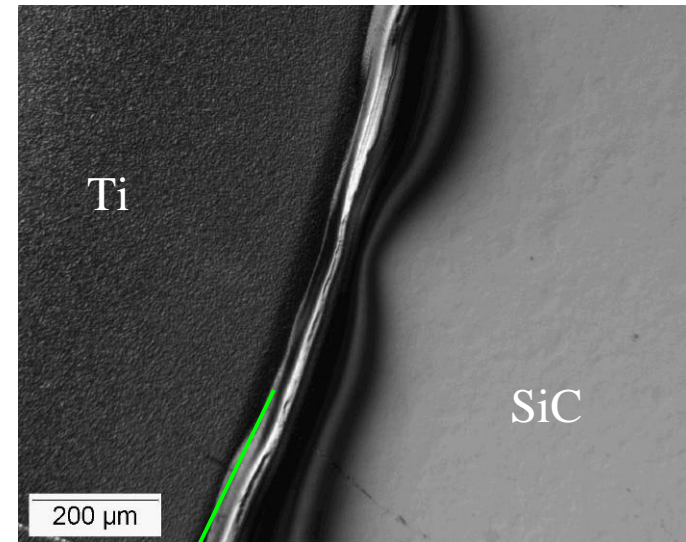


Close-up View of PVD Ti Coatings on SiC Discs

On Less Polished SiC



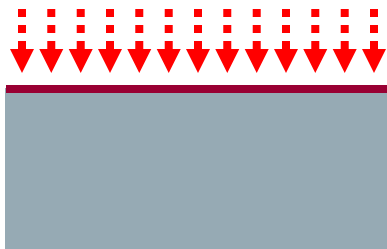
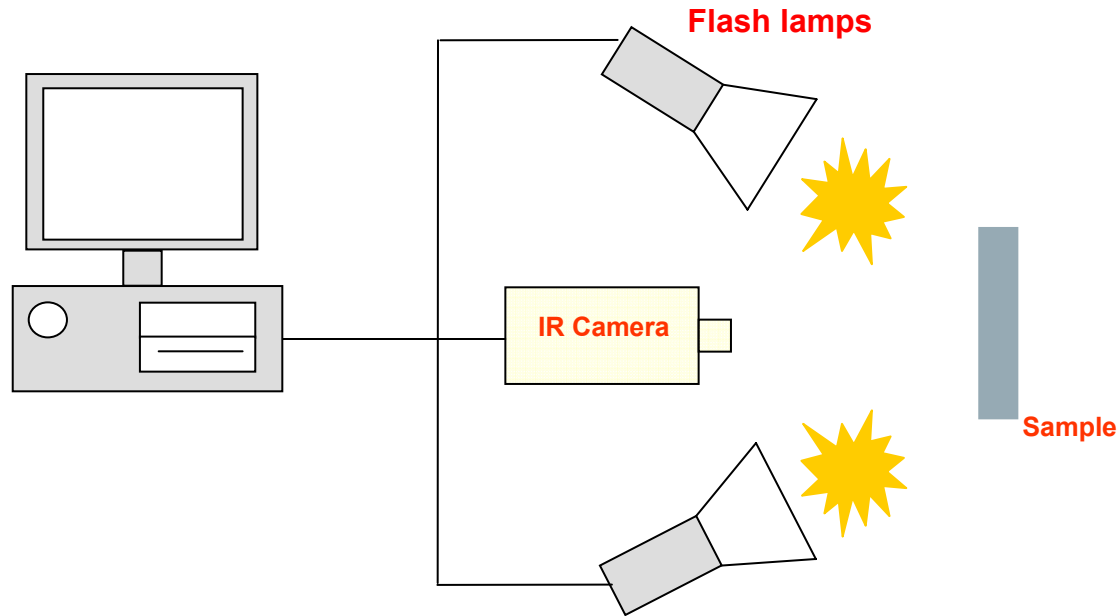
On Highly Polished SiC



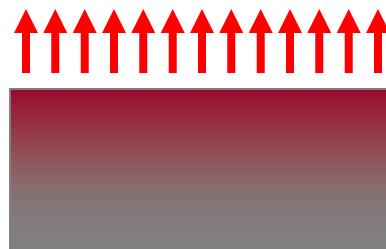
The coating is more dense on the highly polished SiC.



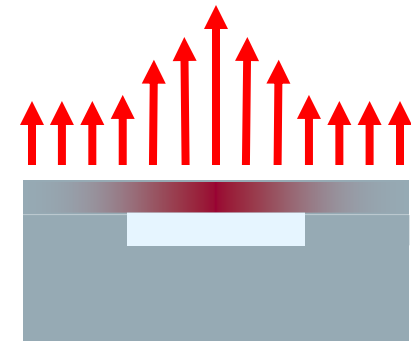
NDE: Pulsed Thermography Overview



Light pulse uniformly heats sample surface



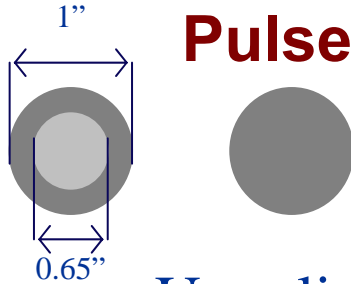
Thermal energy diffuses into the sample and is uniformly emitted from surface



Increase IR radiation at the surface due to the presence of a subsurface defect



Pulsed Thermography Results of Bonded SiC Derivative Images

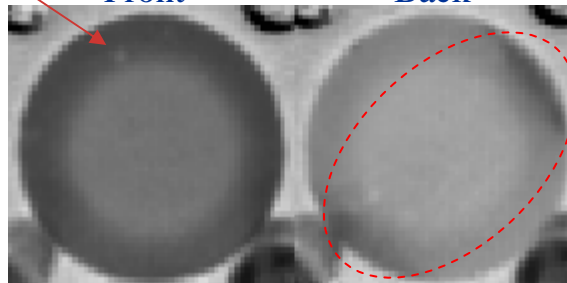


Unpolished

Visible from surface

Front

Back



Run #113/31967 (On 106 Mini Hot Press)
Thermal Derivative Image (0.007 s)



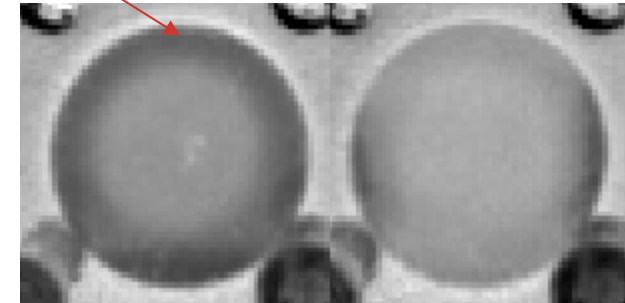
Optical Photos

Polished

Notch on front

Front

Back



Run #114/31967
Thermal Derivative Image (0.007 s)



Optical Photos

- Presence of bonding was detected in the pulsed thermography images from front and back of the SiC disks
- Results regarding bond quality are inconclusive due to surface conditions (i.e. reflections)

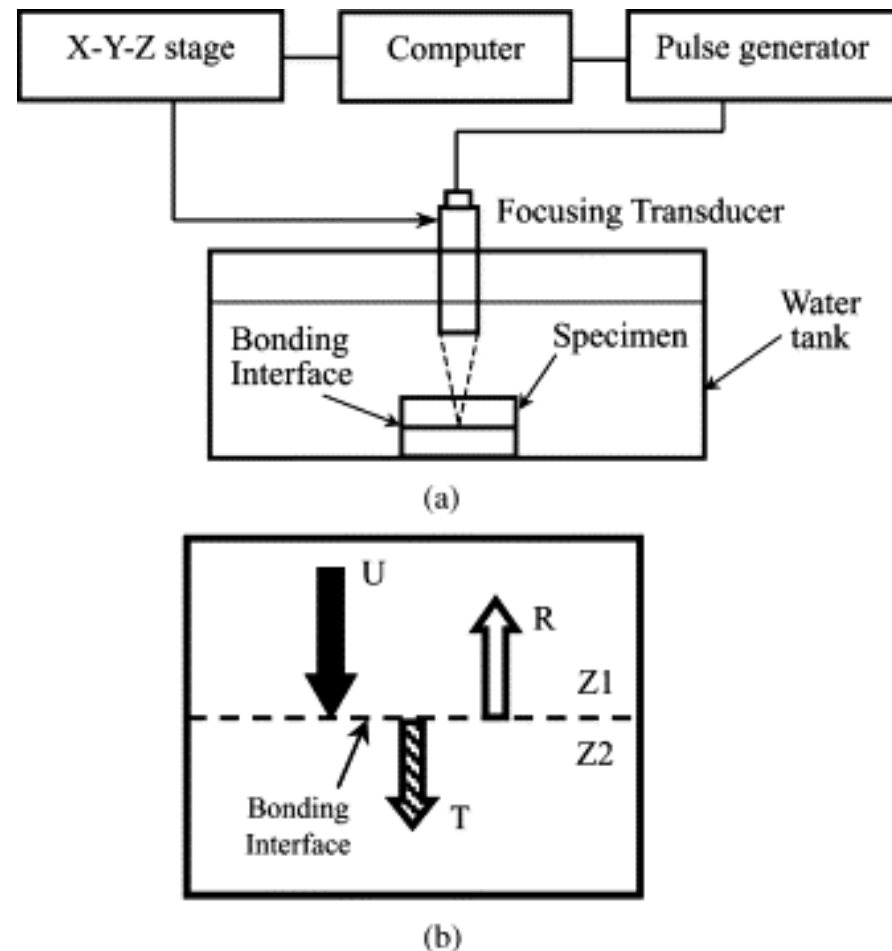
Thermal Parameters:

160x128 portion of focal plane array
Capture rate: 409 Hz
223 frames (0.5 s)



NDE: Immersion Ultrasonic Testing Basics

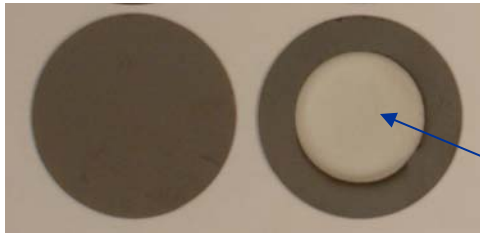
- A high frequency ultrasonic pulse (U) enters specimen.
- Some of the signal is reflected back at the bond interface (R) while the remaining energy is transmitted (T) and eventually reflected at the back surface of the sample.
- The amount of energy reflected at the interface depends on the acoustic impedance (z) mismatch between the materials at the interface.
- Well bonded, similar materials will result in very little or no reflection at the interface while a disbond or air gap will cause more of the energy at the interface to reflect back.





Non-Destructive Evaluation (NDE) Method of Ultrasonic Immersion Shows Very Good Bonding of 1" Discs

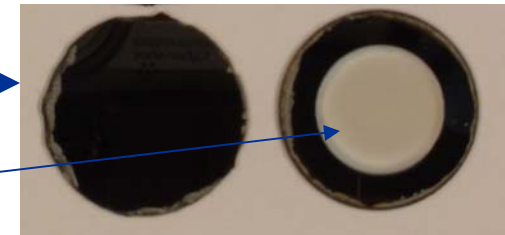
Less Polished SiC



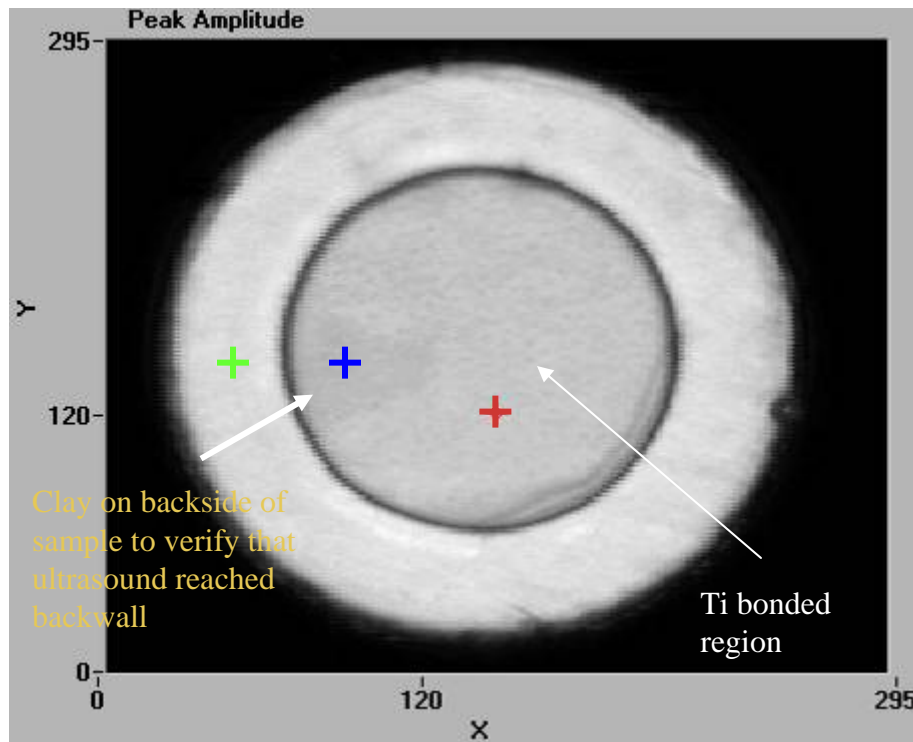
Discs Before Bonding

0.65" Diameter PVD Ti Coating

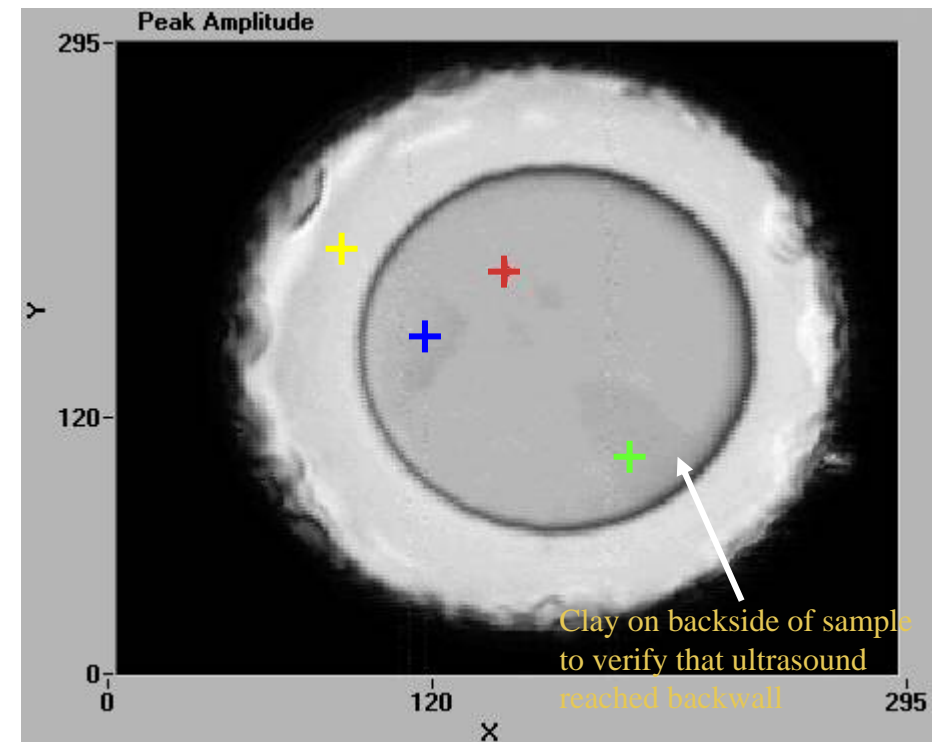
Highly Polished SiC



Ultrasonic C-scan Image of Bonded Discs



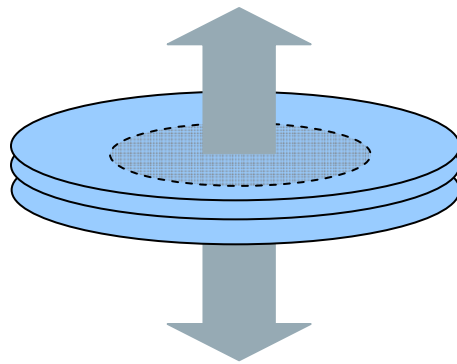
Ultrasonic C-scan Image of Bonded Discs





High Strength of Bonds Greatly Exceed the Application Requirements

1" Diameter Discs with a
0.65" Diameter Bond Area



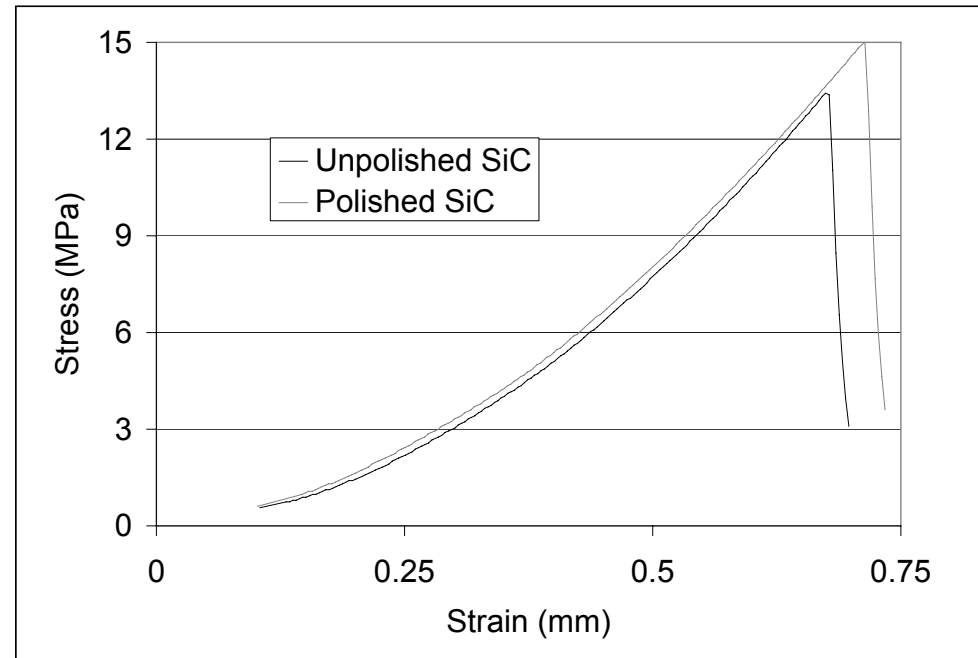
Pull test tensile strengths:

13.4 MPa (1.9 ksi)

15.0 MPa (2.2 ksi)

Slightly higher strength from the highly polished SiC suggest that a smoother surface contributes to stronger bonds or less flawed SiC.

Failures are primarily in the SiC substrate rather than in the bond area.

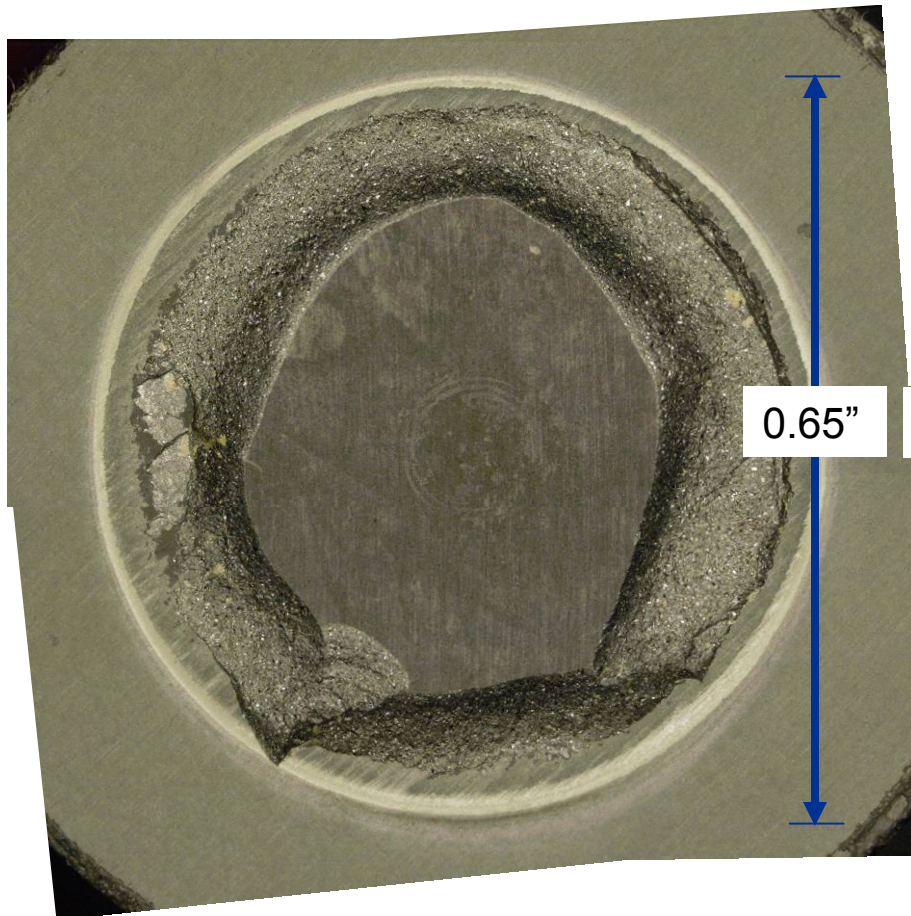


The injector application requires a strength of about 3.45-6.89 MPa (0.5 - 1.0 ksi).



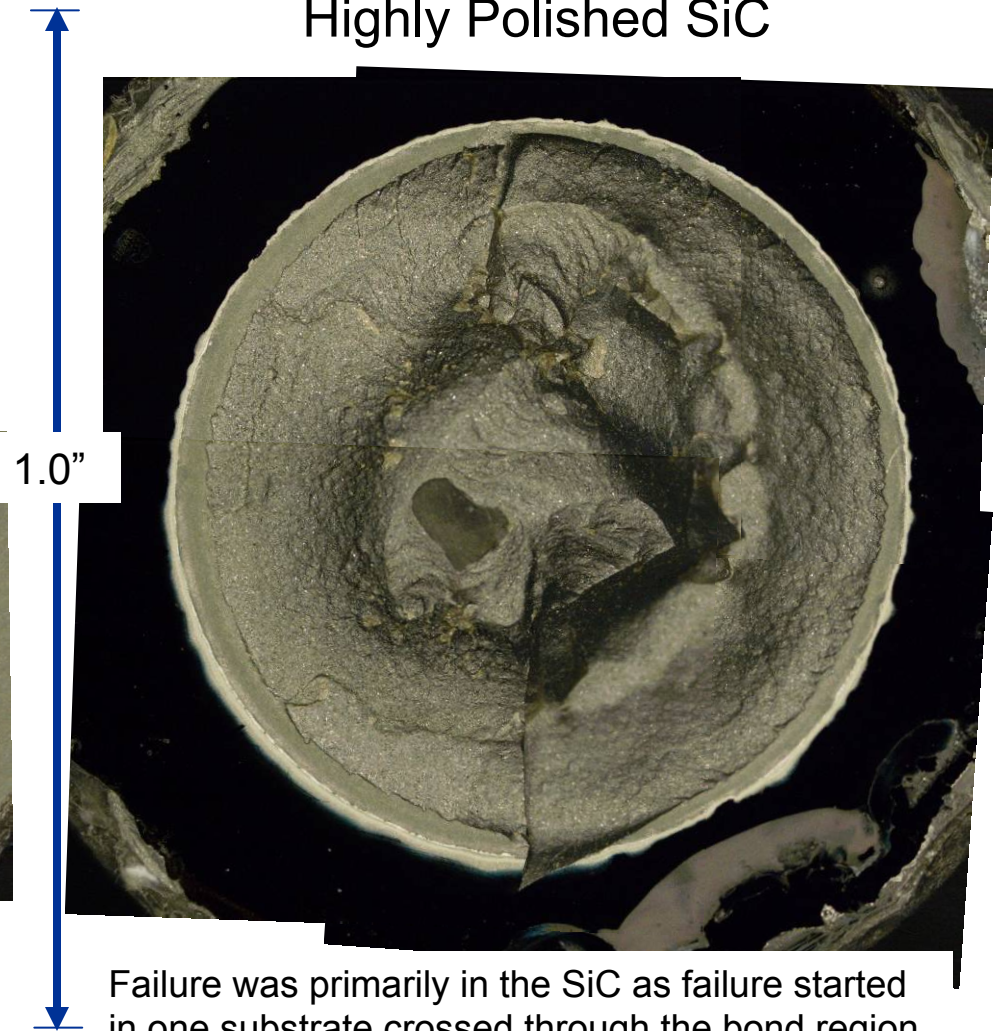
Fracture Surfaces from the Pull Tests of the 1.0" Joined Discs with 0.65" Diameter Bond Region

Less Polished SiC



Failure was in the SiC substrate rather than the bond. The bond was pulled out intact from the failing SiC substrate.

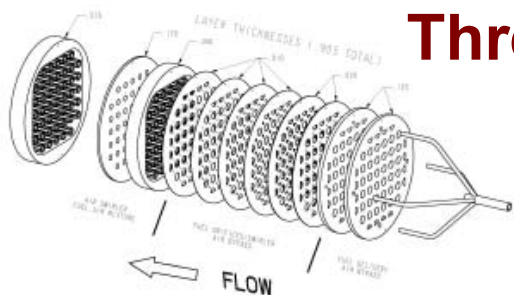
Highly Polished SiC



Failure was primarily in the SiC as failure started in one substrate crossed through the bond region and continued in the other SiC substrate.



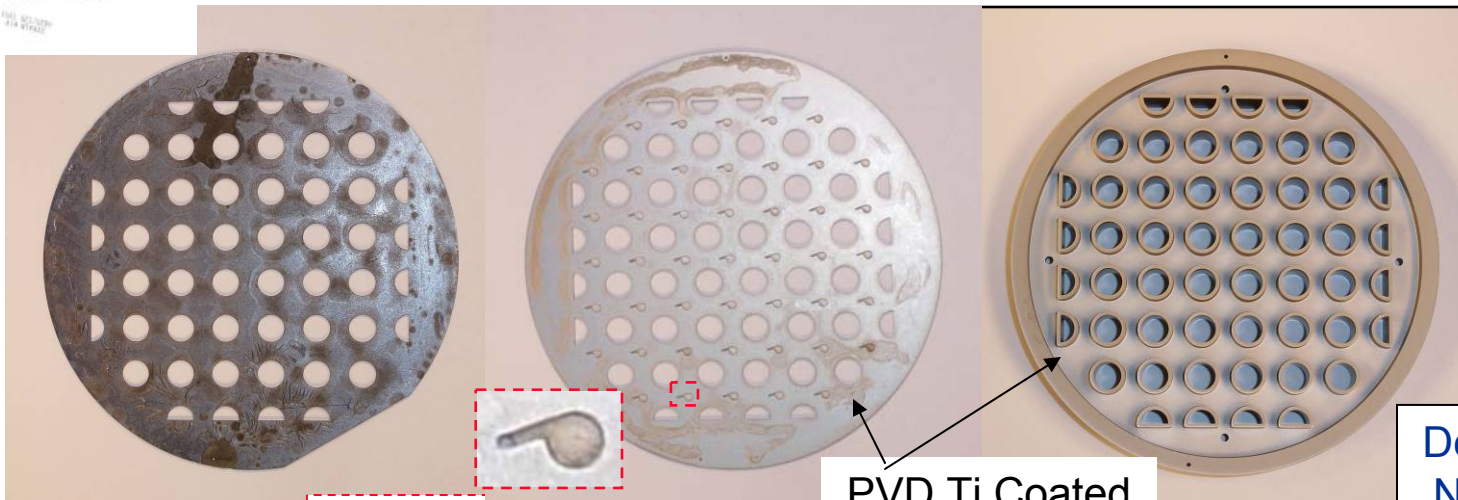
Three Part 10 cm (4") Diameter SiC Injector



Stacking Sequence
Top to Bottom



**Top
Surfaces**

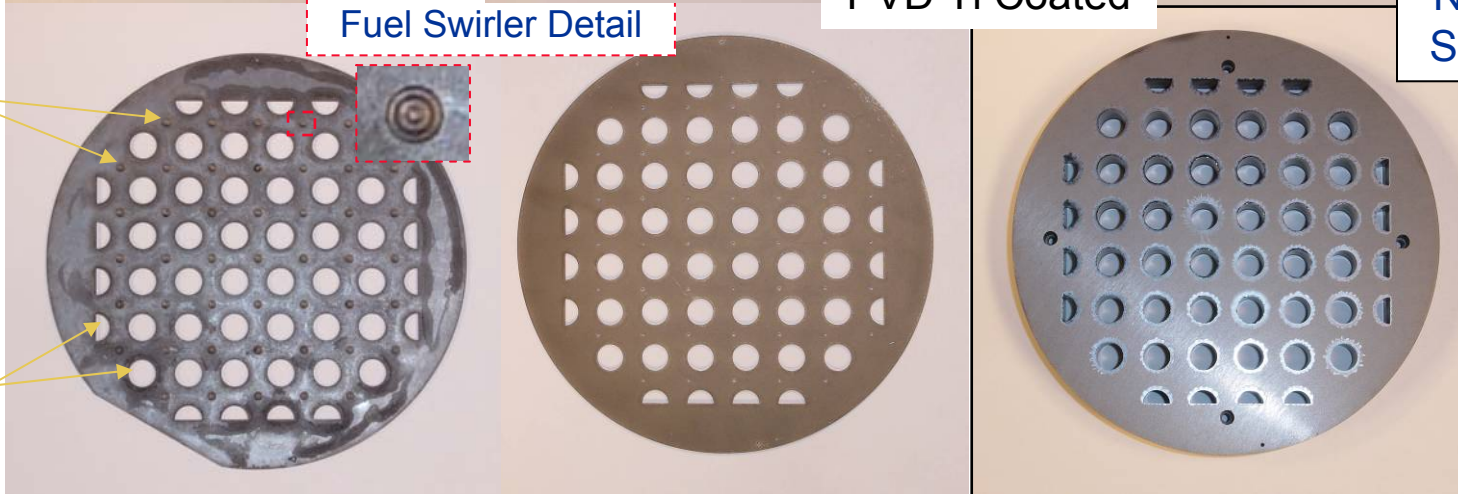


Detail
Next
Slide

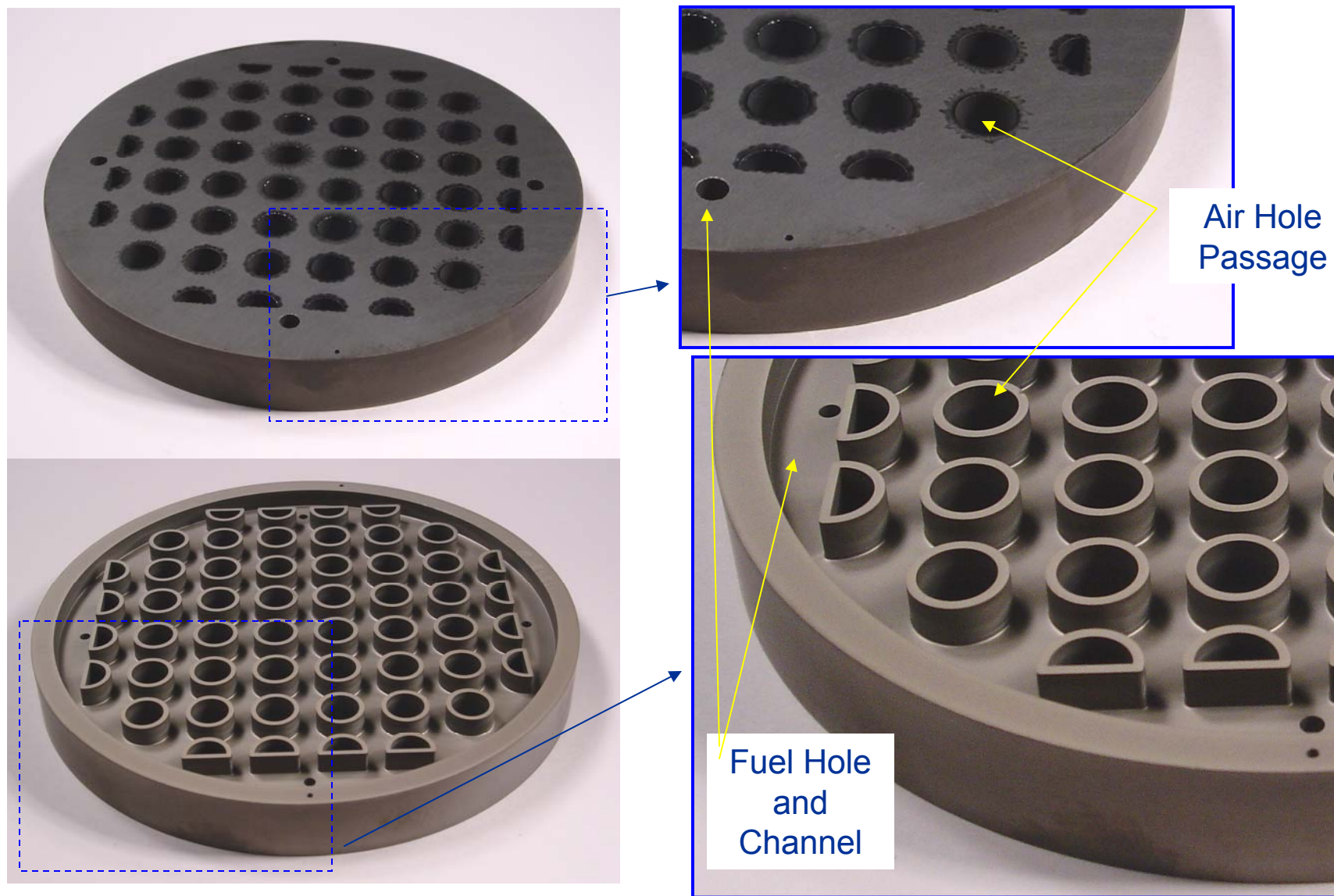
**Small Fuel
Holes**

**Bottom
Surfaces**

**Large Air
Holes**



Detail of the Thickest Injector Substrate (~0.635 cm thick)

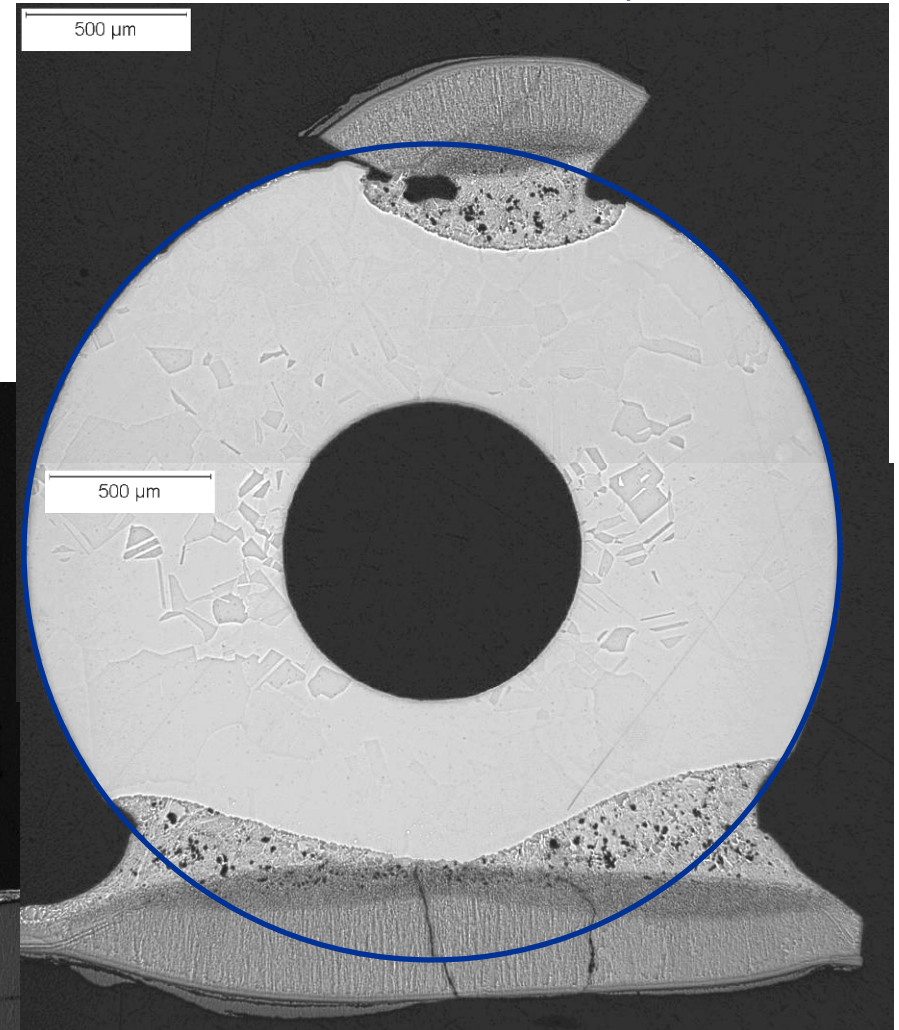
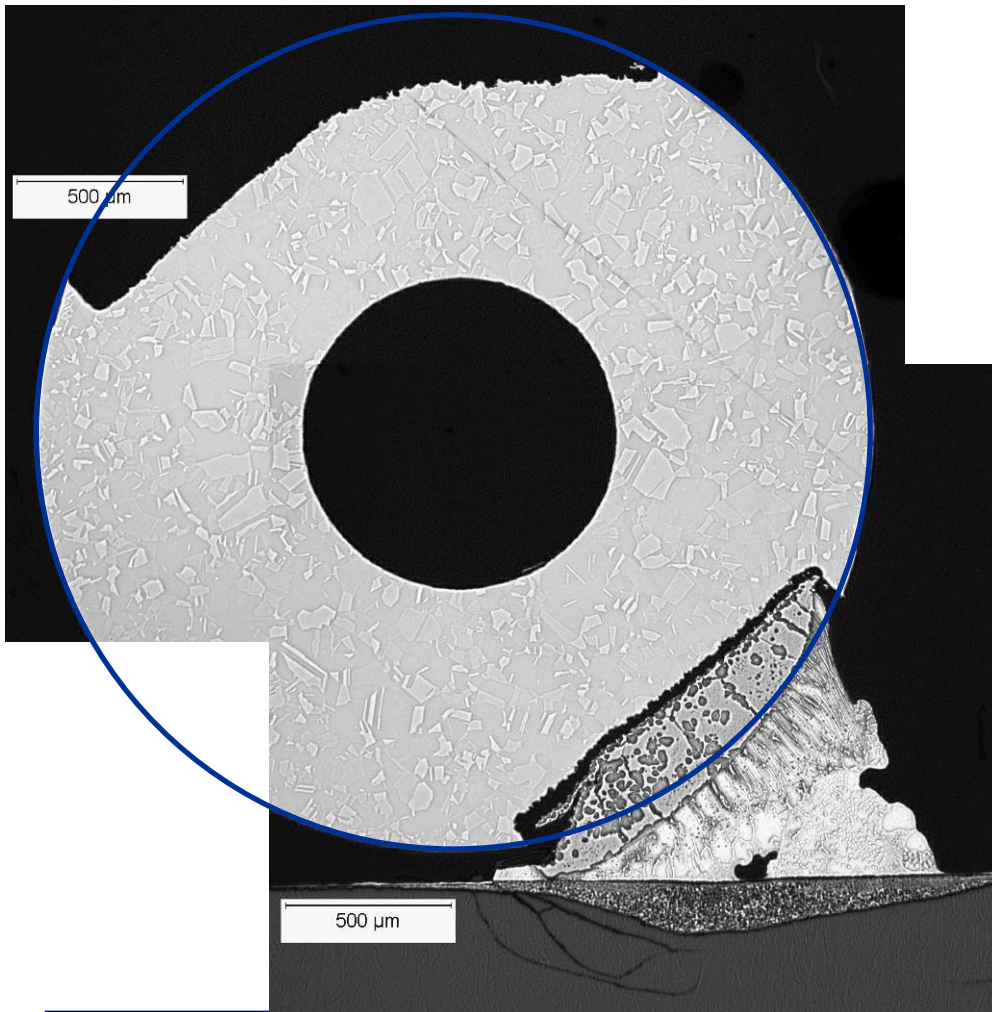




Kovar Tube to SiC Brazing

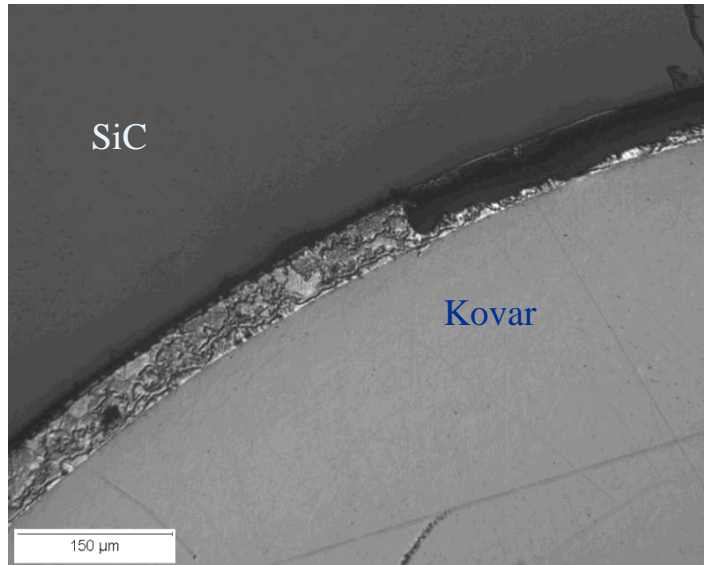
B1 Copper-ABA(L) (Cu-92.75, Si-3.0, Al-2.0, Ti-2.25)

B2 MBF 20 Alloy - AWS BNi2/AMS 4777 (Cr-7, Fe-3, Si-4.5, C-0.006, B-3.2, Ni-balance)

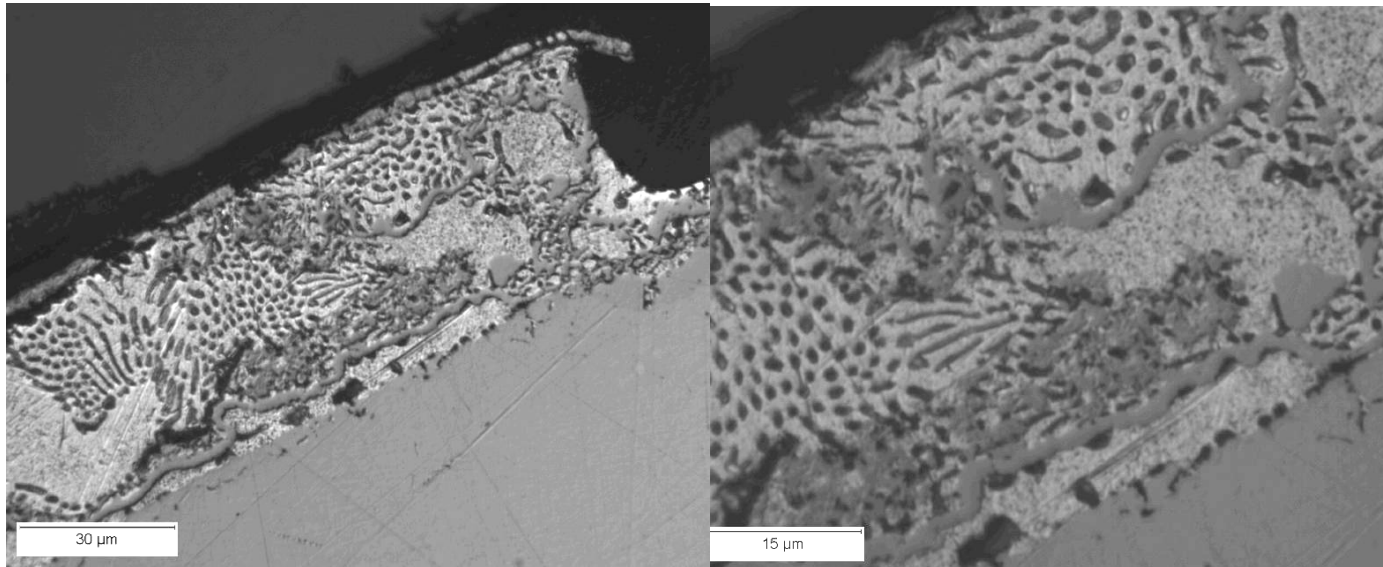


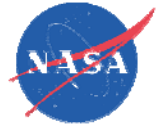


Kovar Tube to SiC Substrate Joining with Ticusil Paste

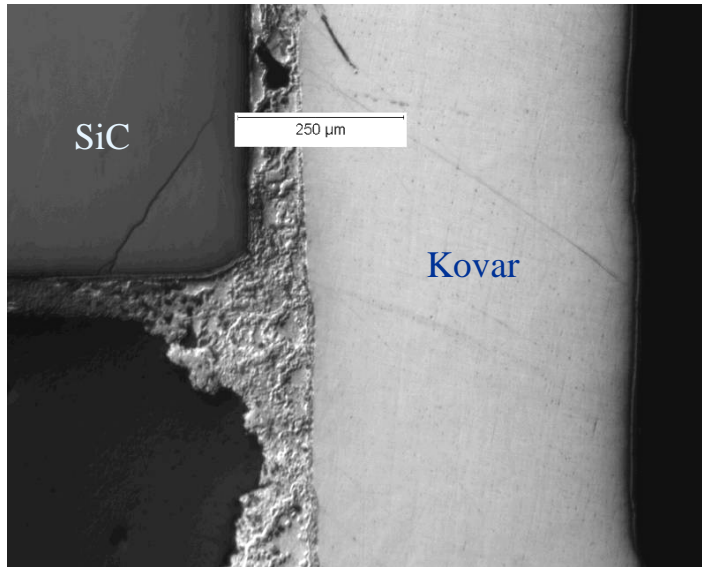


- Sectioned perpendicular to the tube.
- Good reactivity.
- However there was difficulty filling the curved gap with paste.

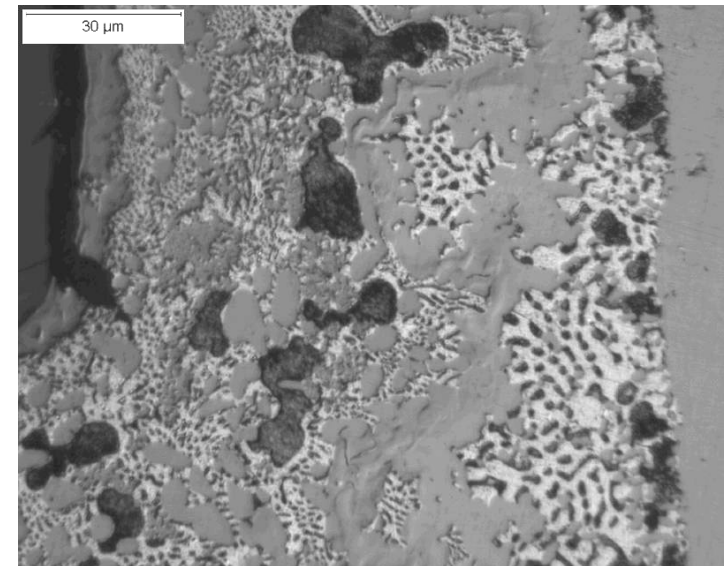
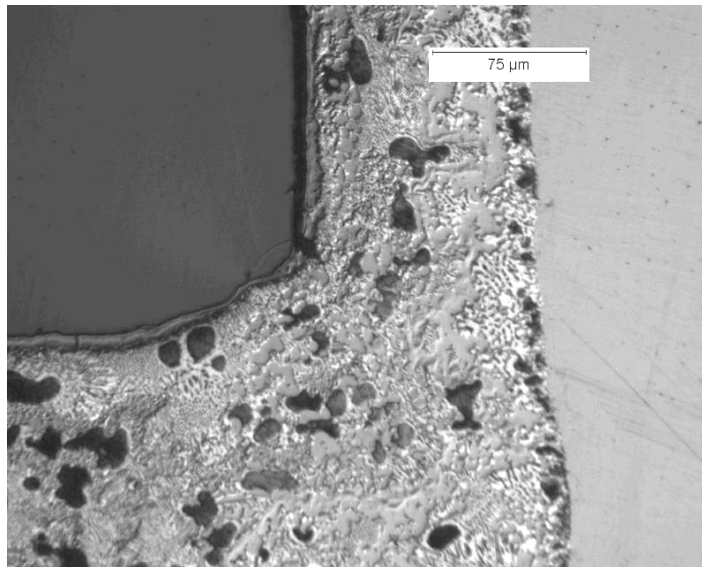




Kovar Tube to SiC Substrate Joining with Ticasil Paste



- Sectioned parallel to the tube.
- Better reactivity and filling than the previous sample.





Future Studies

- Future efforts will further evaluate this bonding method to determine if it is fully capable of meeting the needs of the proposed injector application – uniform, leak-free bonds with stability and strength retention at temperatures up to 800°F.
- Develop and characterize Kovar to SiC joining.
- Apply joining techniques to component fabrication and support in-house component testing.



Summary and Conclusions

- Diffusion bonds fabricated with the alloyed Ti foil as the interlayer formed five to seven phases in the bond.
 - Microcracks due to the formation of thermally anisotropic phases.
- Diffusion bonds fabricated with the 10 micron PVD Ti coating gave better diffusion bonds than the alloyed Ti foil.
 - Fewer and preferred phases were formed which resulted in bonds without microcracks.
- Processing with thinner interlayers and/or for longer durations gave better diffusion bonds.
- NDE method of ultrasonic immersion shows good, uniform bonding.
- Strengths are well above the application requirements.



Acknowledgements

- This effort was supported by the NASA Glenn Research Center under the Subsonics and Supersonics Foundation Research Programs.
- The authors would like to thank the following:
 - Dr. Dan L. Bulzan and Robert R. Tacina at NASA GRC for their support and for providing the injector design and requirements.
 - James Smith of QSS Group, Inc. at NASA GRC for conducting electron microprobe work.
 - Dr. Robert Okojie of NASA GRC for providing PVD Ti Coated CVD SiC.
 - Richard. E. Martin and Laura M. Cosgriff of Cleveland State University for conducting NDE